Final Report

Studies of the role of surface treatment and sizing of carbon fiber surfaces on the mechanical properties of composites containing Carbon Fibers

Kansas NASA-EPSCoR Program

work carried out at
Kansas State University, the University of Kansas and
Wichita State University

Principal Investigator:

Peter M.A. Sherwood, Professor of Chemistry,
Kansas State University, Manhattan, Kansas 66506-3701
Tel: (913)-532-6689
FAX: (913)-532-6666

Co-Principal Investigators:

Kevin B. Lease, Assistant Professor of Mechanical Engineering, Kansas State University, Manhattan, Kansas 66506
James E. Locke, Associate Professor of Aerospace Engineering, 2004 Learned Hall, The University of Kansas, Lawrence, Kansas 66045
John S. Tomblin, Assistant Professor of Aerospace Engineering, The Wichita State University, Wichita, Kansas 67260-0093
Youqi Wang, Assistant Professor of Mechanical Engineering, Kansas State University, Manhattan, Kansas 66506

Final Report

Studies of the role of surface treatment and sizing of carbon fiber surfaces on the mechanical properties of composites containing Carbon Fibers

Kansas NASA-EPSCoR Program

work carried out at
Kansas State University, the University of Kansas and
Wichita State University

Principal Investigator:

Peter M.A. Sherwood, Professor of Chemistry,
Kansas State University, Manhattan, Kansas 66506-3701
Tel: (913)-532-6689
FAX: (913)-532-6666

Co-Principal Investigators:

Kevin B. Lease, Assistant Professor of Mechanical Engineering, Kansas State University, Manhattan, Kansas 66506
James E. Locke, Associate Professor of Aerospace Engineering, 2004 Learned Hall, The University of Kansas, Lawrence, Kansas 66045
John S. Tomblin, Assistant Professor of Aerospace Engineering, The Wichita State University, Wichita, Kansas 67260-0093
Youqi Wang, Assistant Professor of Mechanical Engineering, Kansas State University, Manhattan, Kansas 66506

Table of Contents

Abstract

Carbon fiber reinforced composites are materials where carbon fibers are used to reinforce a matrix to produce a light and strong material with important applications in the aerospace industry. There are many aspects of the preparation of these materials that would benefit from a study which combines the research of groups involved in the production, testing and analysis of these materials, and studies of the basic surface chemistry involved. This final reports presents the results of a project that has developed a collaboration between groups in all three of the major research universities in the State of Kansas, and promises to lead to a collaborative program that covers the major aspects of composite development and application. Sherwood hasl provided initial fiber surface treatment and sizing together with fiber and composite surface analysis; Lease, Tomblin and Wang have worked together toward the goal of preparing pre-preg and fabrication of laminated panels; Locke has developed computational models to evaluate the effect of surface treatment (and chemistry) on mechanical properties; Lease, Tomblin and Wang have worked together to perform all necessary mechanical testing. The research has been focused on materials that would benefit the High Speed Civil Transport (HSCT) program. The group has visited Dr. Howard Maars and his colleagues at NASA Langley, and has focused their studies on the NASA requirements discussed in this meeting. An important development, requested by NASA scientists, has been the acquisition and study of K3B as a matrix material for the composites. The project has led to the successful acquisition and surface analysis of K3B, together with the sucessful deposition of this material onto surface oxidized carbon fibers. Mechanical testing, modelling and the construction of composite preparation equipment has been achieved during the grant period.

Research Plan and Activities

Project Description

1. Description of Research Project

Carbon fiber reinforced composites are materials where carbon fibers are used to reinforce a matrix to produce a light and strong material with important applications in the aerospace industry. There are many aspects of the preparation of these materials that would benefit from a study which combines the research of groups involved in the production, testing and analysis of these materials, and studies of the basic surface chemistry involved. This report describes the result of a project initiated with one year of support from the NASA EPSCoR program that has developed a collaboration between research groups in all three of the major research universities in the State of Kansas, and promises to continue to develop a collaborative program that covers the major aspects of composite development and application. The research has been focused on materials that would benefit the High Speed Civil Transport (HSCT) program. The group has visited Dr. Howard Maars and his colleagues at NASA Langley, and has focused their studies on the NASA requirements discussed in this meeting. An important development, requested by NASA scientists, has been the acquisition and study of K3B as a matrix material for the composites. The project has led to the successful acquisition and surface analysis of K3B, together with the sucessful deposition of this material onto surface oxidized carbon fibers. Mechanical testing, modelling and the construction of composite preparation equipment has been achieved during the grant period. Industrial interaction has been developed with one of the carbon fiber suppliers (Amoco) and the matrix manufacturer (Dupont).

1.1 Polymeric Matrix Composites

Carbon and graphite materials are attractive for high temperature applications since they maintain strength and stiffness above 2500K. They are also amongst the lightest refractory materials known and possess low thermal expansion and high thermal and electrical conductivity. Carbon fibers can be produced with desirable properties including high modulus and high strength. These fibers can be used to reinforce various matrices, including carbon and polymeric matrices. Carbon-carbon composites (carbon fiber reinforced carbon composites - CFRC) are an arrangement of carbon fibers in various configurations held together in a rigid carbon matrix. Polymeric matrix composites (carbon fiber reinforced polymer- CFRP) have the carbon fibers held in a polymer matrix (typically epoxy resin or cyanate ester resin). The carbon fibers lead to improved impact strength and fracture toughness for the composite by resisting cracks which would otherwise propagate through the matrix.

CFRP materials have been prepared most often using an epoxy resin matrix. Other polymers have also been used and in this project the *polyimide K3B, of importance to NASA, has been used.* These materials have been widely used as structural materials, especially in the aircraft

1

and space industries, where the strength-to-weight ratio of such composites is very important. From the early days in the development of such materials the most severe problem was the weak fiber-resin bond, which resulted in very poor mechanical properties (e.g. the interlaminar shear strength (ILS) was poor). In fact it was found that the properties were worse for high modulus fibers. Surface treatment of the carbon fibers used was found to lead to a substantial improvement in fiber mechanical properties and the surface chemistry of the fibers has been found to be the key factor that effects the final mechanical properties of the composite. Surface treatment to alter the inert nature of carbon fiber surfaces has been examined using a number of methods, and Sherwood has studied many of these methods.[1-45] These methods are mainly oxidative in nature. They include chemical "wet" methods (e.g., treating carbon fiber surfaces with nitric acid, potassium permanganate, chromic acid, or sodium hypochlorite, etc.); chemical "dry" methods (e.g., catalytic oxidation, oxidation by air, oxygen, or ozone, radio-frequency plasma treatment, etc.); electrochemical methods (e.g., anodic oxidation in various electrolytes such as nitric acid, ammonium salts, etc.); and coating methods (e.g. pyrolytic graphite, silicon carbide whiskers, nickel coating, etc.). The changes caused by these treatments and the interface between the carbon fiber surface and matrix material can be monitored by surface science methods.

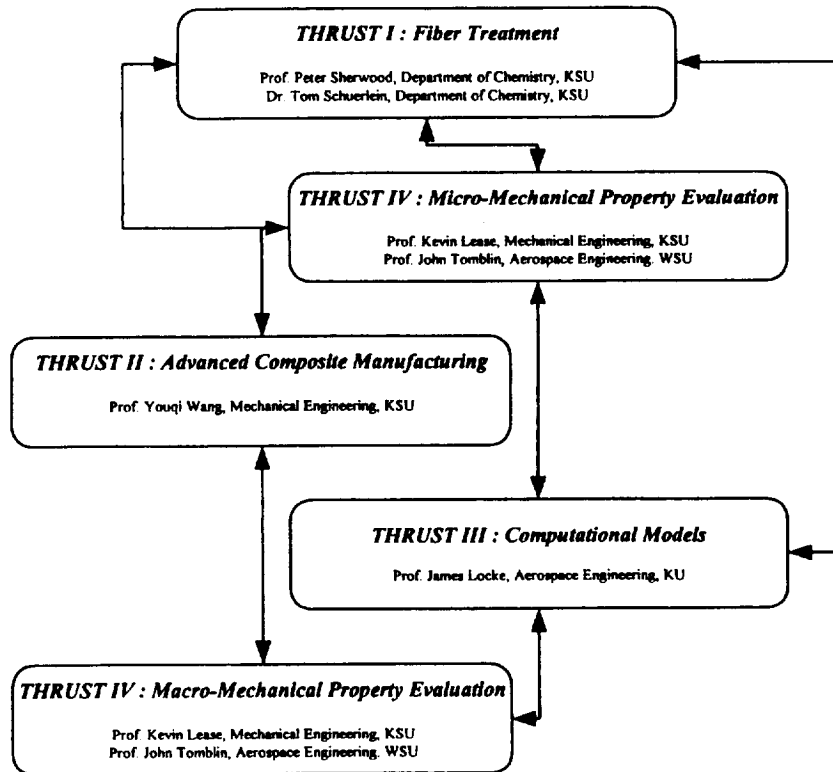## 2. Research Objectives and relevance to the NASA EPSCoR Program

This project is directed towards a study of carbon fiber composite materials which aims to put together a research team that exploits the overall expertise in this area in the State of Kansas. We have done this with the recognition that the best approach is one which brings a wide range of expertise together in order to tackle the substantial challenges presented by these complex, but very important materials. Thus we have included a chemist concerned with the examination of the surface chemistry of carbon fibers (Sherwood), a mechanical engineer (Lease) with experience in the mechanical testing and evaluation of monolithic and composite materials, a mechanical engineer (Wang) with expertise in composite and structural mechanics, an aerospace engineer (Tomblin) with experience in mechanical testing, and an aerospace engineer concerned with computational models for composite materials (Locke). These five personnel are, with the exception of the principal investigator (Sherwood), all at an early, or relatively early stage in building their programs. The project thus allows for the mentoring of the younger faculty that will assist them in developing their own programs, as well as the development of an interdisciplinary research team. We recognize the unique opportunity that the EPSCoR program has to bring faculty and students together from various institutions in the state to pool their talents and resources to enhance the overall research competitiveness of the state. In this proposal we have developed a plan *which none of us could have achieved in our own laboratories*, the project is made possible by such collaborative effort. One of us (Sherwood) already has experience in directing a project involving the three institutions in the NSF EPSCoR program involving faculty working on a "Advanced Materials and Processing" project.

Our objective was to study the mechanical properties of carbon fiber composites, mainly CFRP composites, using an approach that is based upon an understanding and control of each step of the process. Composite materials present special challenges because the surface

2

chemistry of the fibers themselves can have a major effect on the resulting mechanical properties. Thus we have controlled this treatment in a pilot plant in Sherwood's laboratory and have monitored its surface chemistry by X-ray photoelectron spectroscopy, STM and AFM, SEM and wavelength dispersive X-ray spectroscopy in an electron microprobe. We have carried out studies of the mechanical properties of carbon fibers, which will be extended to treated fibers. The pilot plant has the capability to produce enough fiber to produce a composite, a development which was supported by an earlier grant from NASA. The first step in the preparation of a composite is the production of a pre-preg. A pre-preg is a controlled thickness sheet of carbon fiber impregnated with a resin. This is to be prepared in the Mechanical Engineering Department at KSU by Wang, Lease and Tomblin using equipment developed during the course of this project. The location of the chemistry and the mechanical engineering laboratories at KSU allows this step to be done with the minimization of contamination during transfer between laboratories. Lamina and Laminates are being produced by Wang, Tomblin and Lease using the facilities at the KSU mechanical engineering laboratory and/or the National Institute for Aviation Research (WSU) using the pre-preg material produced at KSU and input from Locke. Locke has developed computational micromechanical models to evaluate the effect of surface treatment (and chemistry) on mechanical properties.

Program

We have separated the project into five thrusts. Thrust I has been directed by Sherwood, Thrust II by Lease, Tomblin and Wang, Thrust III by Locke, and Thrust IV by Lease, Tomblin and Wang.

THRUST I : Fiber Treatment
Prof. Peter Sherwood, Department of Chemistry, KSU
Dr. Tom Schuerlein, Department of Chemistry, KSU

THRUST IV : Micro-Mechanical Property Evaluation
Prof. Kevin Lease, Mechanical Engineering, KSU
Prof. John Tomblin, Aerospace Engineering. WSU

THRUST II : Advanced Composite Manufacturing
Prof. Youqi Wang, Mechanical Engineering, KSU

THRUST III : Computational Models
Prof. James Locke, Aerospace Engineering, KU

THRUST IV : Macro-Mechanical Property Evaluation
Prof. Kevin Lease, Mechanical Engineering, KSU
Prof. John Tomblin, Aerospace Engineering. WSU

We have selected the carbon fiber, size and resin to meet the goals of the project. Sherwood's laboratory has obtained experience with a wide range of both PAN based and pitch based carbon fibers with a range of modulii. We are currently using an Amoco THORNEL T-650-42 PAN based carbon fiber. We received approximately 6 lbs of this untreated and unsized fiber from Amoco as an industrial donation to the project. We have received a significant quantity of K3B resin precursor from Dupont, and have also receive IM7 fibers from NASA Langley. IM7 fiber has been chosen to be of the greatest interest to NASA. *We have to tailor our studies so that they would relate to the HSCT program.* This program has presented major design challenges, which cannot be fully met by existing composite materials and provides a major motivation for our studies. The mechanical properties of our composites obtained with fibers that we have subjected to our own surface treatment and sizing will be compared with those of composites prepared with untreated and commercially treated fibers. While commercial treatments are confidential, and can be varied by the manufacturer, the testing of composites prepared from widely available commercial treated fibers will provide a valuable comparison with composites prepared with our own treatment methods.

More details of specific thrust activities are given below:

4

Thrust I : Fiber Treatment

Electrochemical treatment has been carried out using a specially designed treatment line. This line allows control of the surface chemistry which has been monitored by XPS (including studies with monochromatic X-radiation to improve information content and eliminate sample decomposition, X-ray diffraction (XRD), STM, AFM, SEM and wavelength dispersive electron probe microscopy using the approach successfully used for fiber surfaces by Sherwood in previous studies.[1-45] Other techniques have been or will shortly been added. Scanning Auger spectroscopy has just become operational, and it is hoped to have a SIMS facility operational during 1996. Fibers present problems of mounting and can cause instrumental difficulties. One of the X-ray photoelectron spectrometers in Sherwood's group is particularly suited to this work. This spectrometer allows the fibers to be heated to high temperatures, and is fitted with a mass spectrometer to identify gas phase decomposition products.

XPS has proved a powerful method for the investigation of carbon surfaces. The core region (electron binding energies >30eV) is the easiest to interpret since each type of atom has core electrons (electrons that play no significant role in chemical interaction) in a characteristic region, and thus atomic identification is immediate, and information about the chemical environment of each atom is generally provided by the core chemical shift. The valence band region, on the other hand, will give features for all species present in the same energy region. It shows differences that are highly sensitive to the type of material present, since all the energy 7levels are involved in chemical interaction specific to the species studied. Unfortunately core chemical shifts are sometimes unable to distinguish between subtle chemical differences, and the valence band region can thus play an important role. In order to understand the valence band region one needs reliable spectra from model compounds as well as some means of reliably predicting the spectra. Spectral prediction is especially important because many compounds have a surface that does not represent the bulk Sherwood's group has shown the value of valence band XPS as well as core XPS for carbon fiber systems and has developed a range of calculation models that can successfully predict the spectral features.

Figure 1

Figure 1 shows the C1s core XPS spectrum obtained [5] from carbon fibers electrochemically oxidized in solutions of varying pH for 20 minutes using potentiostatic control. Note the chemically shifted C1s features corresponding to different carbon functionality and how these vary with the pH of the electrolyte solution.
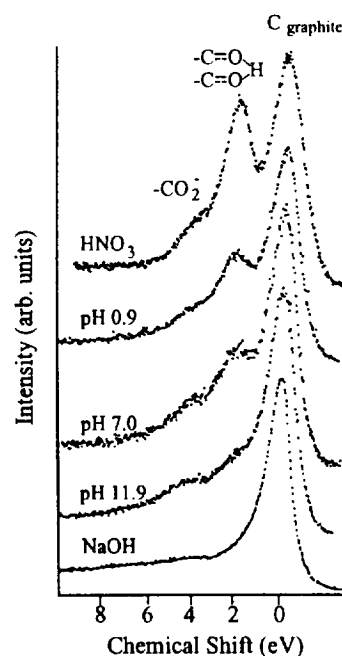
5

The thrust has achieved the following:

- The acquisition of Amoco THORNEL T-650-42 PAN based carbon fiber in an untreated and unsized form from Amoco.
- The acquisition of K3B from Dupont. This material is currently under development at Dupont, and is not available commercially.
- The surface treatment of carbon fibers, including the Amoco THORNEL T-650-42 PAN based carbon fibers.
- The use of monochromatic XPS using an instrument funded by the National Science Foundation for another project, allowed XPS spectra to be ottained of carbon fiber surfaces with a **quality not achieved before**. These better resolved spectra allowed *chemical information to be obtained on carbon fiber surfaces with substantially more confidence* than has been achieved before. These studies are reported in more detail in the Appendix and have been submitted to *Surface and Interface Analysis* for publication. The Appendix contains the full draft of the paper.
- A saturated solution of K3B in 1-methyl-2-pyrrolidinone was prepared (approximately 1% K3B), and this solution was applied to the electrochemically surface oxidized fibers. The results (see report in Appendix) provides *preliminary evidence* for chemical bonding between the surface treated fiber and the resin, suggesting that **this approach may lead to composities with more desirable properties.**
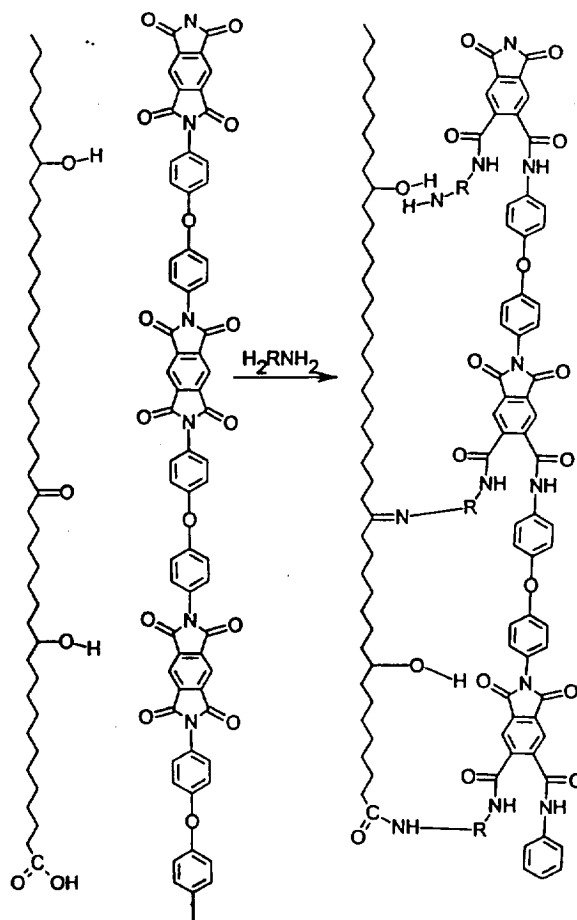

Figure 2

Figure 2 illustrates a model that we are investigating for the possible chemical interaction between a K3B-like matrix material and the surface treated carbon fiber that can be induced by chemical treatment.

Thrust II: Advanced Composite Manufacturing

In this portion of the project, a small affordable system has been developed to fabricate composite specimens with a K3-B matrix.

The processing scheme involves two steps: manufacture of towpregs and manufacture of composite specimens. During the first step, fibers are incorporated into a matrix forming a ready-to-mold tow or sheet, called "towpreg" or "prepreg" respectively. Then, towpregs and prepregs are processed to form composite specimens.

6

Full details are given in the Appendix. The thrust has achieved the following:

- The development of a prepregging system. A yarn spreader has been built to achieve adequate impregnation. The matrix is then applied onto the surface treated and sized fiber via an aqueous foam. The yan then moves though a tube furnace, and the prepreg is then wound on a spool.

- Test runs have been completed on the prepregging system. Test runs have been perfomred on IM7/polyester and E-glass/polyester.

Thrust III - Computational Models

Locke has been responsible for the development of computational models. The computational modeling research objective is to develop micro- and macro-models that directly account for the effects of fiber surface treatment. These models will be used to evaluate the effects of surface treatment (and chemistry) on mechanical properties.

Sherwood has documented that surface chemistry and mechanical properties can be substantially changed by surface treatment. However, it is not well understood how the surface treatments produce these changes[46], and how to incorporate the effects of surface treatment into a mechanical model. One theory is that the surface treatment process reduces the number of surface defects that act as stress risers and cause premature failure. Another concept is based on the assumption that the surface treatment reduces stress concentrations by moving the chemically active boundary zones where the fiber surface bonds to the matrix. This theory assumes that all bonding occurs at boundary zones with no bonding elsewhere. Thus, the stresses are not distributed over the surface of the fiber. To investigate these localized effects, single- and multi-fiber micro- and macro-mechanical models are being developed and compared with the Thrust IV experimental results. Effective properties will be determined based on Thrust I surface analysis results and Thrust IV resin/fiber interface examination.

Several studies[47-50] have used a concentric cylinder model (CCM) to evaluate micro-mechanical stiffness, strength, stresses and strains. The CCM approach involves creating a fiber-matrix model with an interphase region between the matrix and the fibers. Fiber, interphase and matrix are modeled as concentric cylinders. The interphase region is used to model the fiber surface treatment. The effect of a surface treatment can be evaluated by changing the interphase material properties. Carman et al.[49] have used this approach to study the effect of fiber coatings on stress concentrations at the fiber-matrix interface. They demonstrated that minimum stresses and strains can be produced by varying the interphase Young's modulus. All other properties were held constant. The interphase Young's modulus was
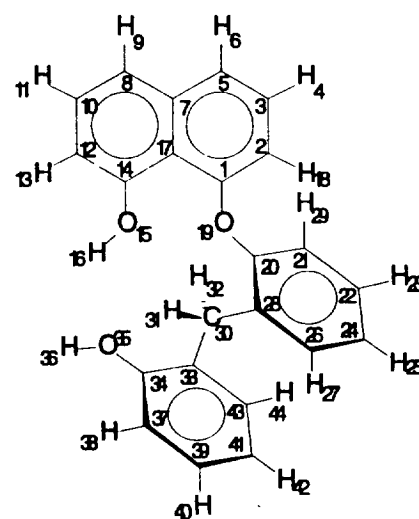

Figure 3

7

also assumed to be a constant (i.e., no variation within the interphase region). An improved version of this approach is proposed for the present study. To study the effect of fiber surface treatment, the interphase properties and dimensions will be treated as variables. The dimensions of the interphase region will be adjusted based on Sherwood's examination of the fiber-matrix interaction. Sherwood can obtain a chemical model of the interfacial interaction between a surface treated fiber (Figure 3) and a matrix resin that can be used to interpret XPS studies of the interphase region.[37] Properties will be determined by comparison with Lease's micro-mechanical test results. Properties within the interphase region will also be allowed to vary. It is emphasized that this approach models the bulk material behavior, not the chemical bonds and individual molecules.

The thrust has achieved the following:
- NASTRAN finite element code has been chosen as a computational modeling tool.
- Preliminary models have been contstructed for two problems:
  (i) a fully three-dimensional CCM.
  (ii) a two-dimensional model.
  The three-dimensional model has been found to be sufficiently refined to determine localized stresses.

Thrust IV: Mechanical Evaluation of Fiber/Matrix Adhesion

This phase of the project involves mechanical testing to evaluate the effect of the fiber surface treatment on the mechanical behavior of the composite material. These tests will be performed on composite specimens manufactured using untreated carbon fibers, commercially treated carbon fibers and carbon fibers treated during Thrust I of this project. This evaluation will be carried out at both the micromechanical and macromechanical levels and will not only provide a comparative evaluation of the fiber surface treatment process but will also provide input properties and experimental verification testing for the computational modeling phase of this project (Thrust III).

Details are provided in the Appendix. The thrust has achieved the following:
- Test equipment is in place and trial tests have been performed.
- Resin and fibers have been obtained.
- Prepreg has been obtained.
- ASTM specimens have been fabricated and tested and nonlinear shear curves obtined.
- A torsion machine has been designed and fabricated.

8

Personnel and Background of the Investigators

Thrust I

Originally this thust was to be supported by a postdoctoral fellow. This person appointed moved to a permanent position during the course of the project, and the project was continued by graduate students.

Faculty: Professor P.M.A. Sherwood
Postdoctoral Fellow: Dr. T. Schuerlein
Graduate Students: Michael A. Rooke
Hema Viswanathan
Nathan Havercroft

Thurst II
Faculty: Assistant Professor Y. Wang
Graduate Student: Manoj Kashiramka

Thrust III
Faculty: Associate Professor J.E. Locke
Graduate Student: Y. Yilmaz

Thurst IV
Faculty: Assistant Professor K.B. Lease
Assistant Professor J. Tomblin
Graduate Students: David Bradford
Kathleen Bowman

Senior Investigators
Each paragraph below summarizes the complementary expertise brought to this proposal by these investigators.

Sherwood has been involved in surface science studies (especially X-ray photoelectron spectroscopy (XPS or ESCA)) since 1972. Sherwood's research group has been investigating the surfaces of carbon fibers since 1975 in a project supported by the U.K. Ministry of Defence from 1975-1986. In 1988-1992 the project was supported by the Fibers Department of the Du Pont Company. In 1992 two major projects involving carbon fiber surfaces started. One, funded by the Air Force Office of Scientific Research involves oxidation protection of carbon-carbon composites, and the other funded by NASA involved the surface chemistry of carbon fiber surfaces. Sherwood is funded by the National Science Foundation for studies of Corrosion and Oxidation, and is PI of a large NSF EPSCoR funded "Advanced Materials and Processing" project.

Lease has had substantial experience in the experimental evaluation of both monolithic and composite materials. This research has included a wide range of deformation tests in support of constitutive modeling as well as fatigue and fracture mechanics related experiments. Lease has also had experience in the macro and microscopic examination of fractured test specimen and material samples.

Locke has a strong background in the areas of finite element structural analysis and composite materials. His research with NASA Dryden focused on the development of analytical

9

methods for heated composite structures (such as the HSCT). He is currently involved in the development of computational design methods for composite structures. The proposed activity will complement and enhance current and previous research by extending methods applied only to marcomechanical behavior to include the effect of micromechanical changes.

Tomblin's background is composed of substantial work both experimentally and analytically dealing with the micromechanical behavior of composites, particularly in compression. In addition, Tomblin has had the opportunity to do a variety of experimental studies characterizing the material behavior and properties of various composite materials ranging from glass/polyester to woven carbon/epoxy materials.

Wang has a broad background in composite mechanics and structural mechanics. From 1988 to 1990, she was supported by the Humboldt Foundation of West Germany for research on the mechanics of metal matrix composites, focusing on the effect of plastic interface zones around fibers on the fracture resistance of fibrous reinforced composites. Since 1991, she has involved herself in the meso-mechanics of 3-D braided composites. Her research is aimed at developing an analytical procedure that links preform design, machine set up design, the manufacturing process and performance evaluation into a closed loop.

References

1. A.Proctor and P.M.A.Sherwood, *J. Electron Spect.* **27**, 39 (1982).
2. A.Proctor and P.M.A.Sherwood, *Carbon* **21**, 53 (1983).
3. A.Proctor and P.M.A.Sherwood, *Surf. Interface Anal.* **4**, 212 (1982).
4. C.Kozlowski and P.M.A.Sherwood, *J. Chem. Soc. Faraday I* **80**, 2099 (1984).
5. C.Kozlowski and P.M.A.Sherwood, *J. Chem. Soc. Faraday I* **81**, 2745 (1985).
6. J.Harvey, C.Kozlowski and P.M.A.Sherwood, *J. Mat. Sci.* **22**, 1585 (1987).
7. C.Kozlowski and P.M.A.Sherwood, *Carbon* **24**, 357 (1986).
8. C. Kozlowski and P.M.A. Sherwood, *Carbon* **25**, 751 (1987).
9. Y. Xie and P.M.A. Sherwood, *Appl. Spect.* **43**, 1153 (1989).
10. Y. Xie and P.M.A. Sherwood, *Chem. Mater.* **1**, 427 (1989).
11. Y. Xie and P.M.A. Sherwood, *Chem. Mater.* **2**, 293 (1990).
12. Y. Xie and P.M.A. Sherwood, *Appl. Spect.* **44**, 797 (1990).
13. Y. Xie and P.M.A. Sherwood, *Chem. Mater.* **3**, 164 (1991).
14. Y. Xie and P.M.A. Sherwood, *Appl. Spect.* **44**, 1621 (1990).
15. Y. Xie and P.M.A. Sherwood, *Appl. Spect.* **45**, 1158 (1991).
16. Y. Xie, T. Wang, O. Franklin and P.M.A. Sherwood, *Appl. Spect.* **46**, 645 (1992).
17. P.M.A. Sherwood, *Mater. Res. Soc. Proc.*, **270** (Novel forms of Carbon), 79-89 (1992).
18. A. Al-Sharif, M.J. O'Shea, S.Thomas and P.M.A. Sherwood, *J. Appl. Phys.* **67**, 5023 (1990).
19. A. Proctor and P.M.A. Sherwood, *Anal. Chem.* **52**, 2315 (1980).
20. A. Proctor and P.M.A. Sherwood, *Anal. Chem.* **54**, 13 (1982).
21. P.M.A.Sherwood and A.Proctor, <u>Studies of the Surface of Carbon Fibres</u>, Final Report 1977-1980, (Defence Research Information Centre.,U.K., 1982).
22. Y. Xie, T. Wang, M.A. Rooke and P.M.A. Sherwood, *Surface Science Spectra*, **2**, 210, 1992.
23. Y. Xie and P.M.A. Sherwood, *Surface Science Spectra*, **2**, 204, 1992.
24. Y. Xie and P.M.A. Sherwood, *Surface Science Spectra*, **2**, 198, 1992.
25. Y. Xie and P.M.A. Sherwood, *Surface Science Spectra*, **2**, 192, 1992.
26. Y. Xie and P.M.A. Sherwood, *Surface Science Spectra*, **3**, 306,1992.
27. Y. Xie and P.M.A. Sherwood, *Surface Science Spectra*, **2**, 216, 1992.
28. Y. Xie and P.M.A. Sherwood, *Surface Science Spectra*, **3**, 253,1992.
29. Y. Xie and P.M.A. Sherwood,*Surface Science Spectra*, **2**, 222, 1992.
30. Y. Xie and P.M.A. Sherwood, *Surface Science Spectra*, **3**, 259,1992.
31. Y. Xie and P.M.A. Sherwood, *Surface Science Spectra*, **3**, 265,1992.
32. Y. Xie, T. Wang and P.M.A. Sherwood, *Surface Science Spectra*, **3**,247,1992.
33. Y. Xie, T. Wang and P.M.A. Sherwood, *Surface Science Spectra*, **3**,271, 1992.
34. Y. Xie and P.M.A. Sherwood,*Surface Science Spectra*, **4**,367,1992.
35. C.L. Weitzsacker, M.Bellamy, and P.M.A. Sherwood, *J. Vac. Sci. Technol. A*, **12**, 2392, 1994.
36. Y. Xie and P.M.A. Sherwood, *Chem.Mater.*, **6**, 650, 1994.
37. T. Wang and P.M.A. Sherwood, *Chem. Mater.*, **6**, 788, 1994.
38. M.A. Rooke and P.M.A. Sherwood, *Surf. Interface Anal.*, **21**, 681, 1994.
39. P. M.A. Sherwood, invited review paper for a special issue of *J. Electron Spectrosc.* in press.
40. M.A. Rooke and P.M.A. Sherwood, *Carbon*, **33**, 375, 1995.
41. M.A. Rooke, J.A. Rotole and P.M.A. Sherwood, *J. Vac.Sci. Technol., A,* **13**, 129, 1995.
42. T.Wang and P.M.A. Sherwood, *Chem.Mater.*, **7**, 1029, 1995.
43. C. L. Weitzsacker and P.M.A. Sherwood, *Surface Interface Anal.*, **23**, 551, 1995.

44 T. Wang and P.M.A. Sherwood, *Surf. Interface Anal.*, **23**, 659, 1995.

45 T. Wang and P.M. A. Sherwood, *Chem. Mater.*, **7**, 1031, 1995.

46 S. M. Lee, *Handbook of Composite Reinforcements*, pp. 104-105, VCH Publishers, 1993.

47. N.J. Pagano and G.P. Tandon, *Composites Science and Technology*, **31**, 273, 1988.

48. N. J. Pagano, *IUTAM Symposium on Local Mechanics Concepts for Composite Material Systems*, Blacksburg, Virginia, 1991.

49. G.P. Carman et al., *J. Composite Materials*, **27**, 589, 1993.

50. G.P. Tandon, *J.Composite Mater.*, **29**, 388, 1995.

51. **The space available has prevented us from providing an extensive review of the literature, and most of the references are from our own work. However our own references contain many citations of the work of other researchers in the field.**

Appendix: Detailed Reports

Thrust I : Fiber Treatment

Submitted to Surface Interface Analysis

X-Ray Photoelectron Spectroscopic Studies of Carbon Fiber Surfaces.

21. Comparison of Carbon Fibers Electrochemically Oxidized in Acid using Achromic and Monochromatic XPS

Hema Viswanathan, Michael Rooke[†] and Peter M. A. Sherwood[*]

Department of Chemistry, 111 Willard Hall, Kansas State University, Manhattan,

Kansas 66506-3701, U.S.A.

Abstract

Amoco M40 PAN-based carbon fibers were electrochemically oxidized in a pilot plant system. The changes in the surface of the fibers were monitored using monochromatic X-ray photoelectron spectroscopy (XPS). A parallel experiment using achromic X-radiation was conducted for comparison. Other graphitic materials were also studied. Significantly reduced amounts of decomposition of the fiber due to X-ray exposure were observed using the monochromator. The use of monochromatic x-radiation produced considerable narrowing in the linewidth of the graphitic peak. This allowed the curve fitting of the component peaks to be performed with significantly greater confidence.

* Author to whom correspondence should be addressed.

† Present address: Department of Chemistry, University of Hartford, Connecticut 06117.

13

INTRODUCTION

Carbon fibers find extensive use in the manufacture of composite materials due to their high strength, high stiffness-to-weight ratios, resistance to corrosion and stability at elevated temperatures. [1-4] The mechanical properties of these composites are extremely dependent on the surface chemistry of the fiber. Surface treatment of the carbon fibers is found to improve the properties of the composite significantly. [5,6] Electrochemical oxidation is a method widely used for the surface modification of these fibers. The study of the resultant changes in the surface chemistry is an area in which a number of systematic studies have been carried out in our research laboratory (many of which have been identified by "part numbers" to help the reader follow the series of papers sequentially). [7-21] XPS has been widely used for the study of carbon fiber surfaces, there being around 275 papers published in this area. Rather than refer to this large number of references in this paper, the reader is directed to reference 21 and references listed therein. In previously reported work,[8,18] it has been shown that electrochemically oxidized fibers undergo significant decomposition on prolonged exposure to X-rays during an XPS analysis. This is especially important with regard to valence band data where longer collection times are required. This work shows that this decomposition can be essentially eliminated by using a monochromator.

XPS core studies have been widely used to determine the functionality on a particular carbon fiber, and we have found that these studies can be complemented by XPS valence band studies. The correct identification of the surface functionality, and the experimental conditions needed to achieve a particular surface functionality are very important if composites are to be prepared with the desired mechanical and other properties. This is why there have been so many studies of carbon fibers surfaces using a wide range of fiber surface treatments. The

particular type of surface functionality can be very important in leading to beneficial fiber-matrix interactions, and we have found that one can tailor the surface chemistry at the interface to react the fiber with the matrix material, leading to enhanced composite properties.

The use of a monochromator eliminates the X-ray satellites and the Bremstraahlung radiation associated with normal achromic X-radiation. It also results in a significantly narrower $K\alpha_{1,2}$ X-ray linewidth. The narrower linewidth gives XPS data, which when analyzed at high resolution, can reveal previously unresolved features in the XPS spectra. Monochromators have been available on commercial instruments since the mid 1970s, so the benefits of using this radiation source are clear. However the majority of XPS data (including most studies of carbon fibers) are collected with achromatic radiation, and when monochromatic radiation is used it is often used without using the maximum instrument resolution. This is understandable since the use of monochromatic radiation requires longer acquisition times, and high resolution studies can be especially time consuming. The purpose of this work is to show that the use of monochromatic radiation for the study of carbon fibers can lead to considerable improvement in resolution and the near elimination of sample decomposition that allows the surface chemistry to be determined with greater confidence. The enhanced resolution leads to a significant reduction in the linewidths of chemically shifted species that enable one to see features in the spectra that are not identifiable when achromatic XPS is used.

The surface chemistry of the electrochemically oxidized fibers was monitored using monochromatic X-ray photoelectron spectroscopy. The same experiment was also performed using achromatic X-radiation. Other graphitic materials were also studied for comparative purposes.

EXPERIMENTAL

The Amoco M40 carbon fibers, previously unsized and untreated, were oxidized in a pilot

plant system, details of which have been published earlier.[22] The carbon fibers were oxidized in

the galvanostatic mode using 1 M nitric acid solution as the electrolyte. The speed at which the

fibers moved in the plant was kept constant so that the dwell time for all parts of the fiber tow

was 40 seconds. The fibers were oxidized at different values of current, from 0.25 A to 1.00 A.

The fibers were found to degrade at currents higher than 1.00 A. Fiber samples were taken from

different sections of the oxidized fiber tow, dried and analyzed in the X-ray photoelectron

spectrometer.

XPS Experiments

The fiber samples were analyzed in a VSW HA150 X-ray photoelectron spectrometer (150

mm hemispherical analyzer), equipped with a 16-plate multichannel detector system and using

Al Kα X-radiation (300 W) produced from a 32-quartz crystal VSW monochromator. This

instrument operates at base pressures of less than 10^{-9} torr. The X-ray line width is less than 0.18

eV. The same instrument also has an achromic Mg Kα X-radiation source (300 W) with a line

width of about 0.75 eV. This source was used to perform the achromatic study on the fiber

samples. The spectrometer was operated in the fixed analyzer transmission (FAT) mode with a

22eV pass energy, and the same pass energy was used for all the monochromatic and achromatic

XPS studies. The same lens magnification was used in both monochromatic and achromatic

studies, so that the same sample area was probed in each case. The spectrometer energy scale

was calibrated using copper [31] and the C1s binding energy of the graphitic peak was fixed at

284.6 eV for calibration purposes.

Curve fitting of core XPS spectra was carried out using a non-linear least-squares fitting

program with a Gaussian-Lorentzian product function [23] and a non-linear background.[34] The G/L

16

mix was taken as 0.5 for all peaks except the main graphitic peak, which was taken as 0.8 and included an exponential tail.

Calculations.

The graphite band structure calculation was performed using a modified version of the program CRYSTAL (QCPE 577) using an STO-3G basis set. All calculations were performed on an IBM RISC/6000 computer. The density of states were adjusted by the Schofeld cross section values.[26] This adjusted density of states was convoluted with a 1.5eV FWHM 50% Gaussian-Lorentzian product function [32] to give the calculated spectra which is compared with the experimental spectrum below.

RESULTS AND DISCUSSION

This study focused on the study of graphitic materials using XPS excited by monochromatic X-radiation and a comparison of the results of XPS excited by achromatic X-radiation for the same samples. Since achromatic XPS can lead to sample decomposition (see below), the achromatic XPS analysis was performed *after* the monochromatic XPS analysis on the same sample in the same instrument. In addition, the electrochemical oxidation of carbon fibers was also studied using a comparative monochromatic/achromatic XPS analysis. The aim was to show that monochromatic XPS could reduce the effective linewidth of the C1s spectra to the extent where previously ambiguous features can be clearly resolved out. In addition, the decomposition of the fibers normally seen with the use of achromic X-radiation is essentially eliminated when a monochromator is used. The sample designations specified in Table 1 are used throughout this paper. Sample (a) represents the untreated M40 carbon fiber while samples (b)- (e) correspond to the electrochemically oxidized fiber.

The achromic X-rays (hv=1253.6 eV) do not probe as deeply into the surface as the

17

monochromatic X-radiation (hv=1486.6 eV). This is due to the fact that the kinetic energy of the electrons excited by Mg Kα X-rays is lower than that of the electrons excited by the Al Kα X-radiation used in the monochromator.

X-ray Photoelectron Spectroscopic studies of Graphitic Materials

This part of the study dealt with the surface analysis of various graphitic materials. The three samples studied are listed in Table 2. Sample (a) represents highly-ordered pyrolytic graphite (HOPG). Samples (b) and (c) represent pitch-based E-120 carbon fibers and PAN-based Type II carbon fibers respectively. Previously reported work has shown that HOPG produced the narrowest lines for the main C1s peak in graphitic materials and that E-120 most closely resembled HOPG in graphitic character[20] giving a slightly narrower C1s peak. Figure 1 shows the C1s spectra for these materials, using both monochromatic as well as achromic radiation. E-120 fibers produced a linewidth of about 0.96 eV which was reduced to 0.32 eV using a monochromator. The PAN-based fibers, which do not show as much graphitic character as the E-120 pitch-based fibers, produced much broader peaks with achromic radiation. These were narrowed to about 0.4 eV using monochromatic XPS. The HOPG sample had a comparable linewidth (0.32 eV) to the E-120 fibers when monochromatic radiation was used. The achromic spectrum for the HOPG sample shows a much broader feature, perhaps because it is more sensitive to radiation damage than the other carbon materials. The valence band shows comparable levels of O2s feature at 24 eV, so the extra linewidth is not due to more oxidation. We have reported the considerable line broadening that can occur in the C1s region after exposure to ion bombardment, [6] and it may be that the Bremstraahlung radiation, and the extra electron presence when using achromatic radiation gives rise to such damage.

18

The valence band spectra for these samples are also shown in figure 1. Distinct features that are unresolved in the achromic experiment can be clearly seen when the monochromator is used. The valence band spectra of the most graphitic material, HOPG, can be compared with a calculated spectrum obtained from a band structure calculation of the graphite lattice. This calculation was performed on a two-dimensional graphite lattice with a lattice constant of 0.2462 nm with a P6mm two dimensional hexagonal lattice. Figure 2 compares the experimental valence band spectrum of HOPG after removal of a non-linear background[32] with the spectrum generated from the density of states for each orbital type adjusted by the photoelectron cross section and convoluted with an experimental X-ray function. One notes the generally good agreement, and in particular the agreement between the two features around 18 and 14 eV in the experimental and calculated spectrum. The feature around 14eV corresponds to a maximum in the density of states.

Electrochemical Oxidation Results

Survey Spectra. The overall XPS spectra for the electrochemically oxidized M40 fibers are shown in figure 2. The spectra in figure 2(i) were collected using monochromatic Al Kα X-radiation while those in figure 2(ii) were collected using achromic Mg Kα radiation on the same instrument. The untreated fiber shows a dominant C1s line and very little surface oxidation in the monochromatic case. Slightly more oxidation is seen in the achromic case. This is due to the presence of small amounts of chemisorbed oxygen and this is more readily detected when the more surface-sensitive Mg achromic X-radiation is used. The electrochemically oxidized fibers show substantial oxidation, represented by an intense O1s signal in the survey spectra in both the achromic and monochromatic case. At higher oxidation levels (samples (d) and (e)), features

corresponding to the presence of small amounts of iron, chromium and nickel are seen. This is due to some contamination from the stainless steel rollers used to make electrical contact in the pilot plant where oxidation was conducted. This contamination appears to be unavoidable, since metal rollers are required to maintain electrical contact during electrochemical oxidation. Once again, this contamination is seen to a larger extent in the case of the achromic experiment, due to its greater surface sensitivity. Significant amounts of nitrogen are not seen in the survey region. The amounts of oxygen seen in the achromatic radiation spectrum (see also Table 3) are somewhat less in most cases than that seen with monochromatic radiation, even though the latter source would be expected to see more deeply into the surface. This is probably caused by the reduction of oxygen content in the oxidized samples from sample decomposition when the achromatic source is used (see below).

A measure of the relative amounts of C and O can be made if the region of the fiber analyzed by XPS is assumed to be homogenous. While this is a gross approximation that is certainly not correct for the C-O functionality will be greatest in the outer surface region, it does give a qualitative guide to the C/O levels (Table 3).

C1s Spectra. The C1s spectra for the untreated and oxidized fibers are shown in figure 4. Figure 4(i) represents data collected using the monochromator while the spectra in figure 4(ii) used achromic radiation. The spectra for the untreated M40 fiber show a narrow intense peak at 284 eV. This corresponds to the graphitic peak of the carbon fiber. The monochromatic spectrum shows an unusually narrow peak having a full-width at half-maximum (fwhm) of about 0.35 eV. In addition, other functionalities are also seen and these are assigned binding energies as shown in Table 4, which were taken from previous studies.[13, 25] The C1s region was then

20

fitted to component peaks to give the fitted spectra seen in figure 3.

Figure 3(a) shows the fitted C1s spectrum for the untreated M40 fiber, using monochromatic radiation. This spectrum shows the characteristically narrow graphitic peak. In addition, there is a distinct feature at a separation of about 0.7 eV. This corresponds to the β-peak, which occurs for carbon atoms which are attached to (oxidized) carbon atoms whose binding energy is shifted by being bonded to oxygen species. The data in figure 4 (where the β-peak was not identifiable as a shoulder as in Figure 3) were fitted so that the separation of the β-peak was fixed to 0.7 eV. In previous work on electrochemically oxidized fibers, the presence of this β-peak could only be shown as a result of curve-fitting.[5,11,12] Since curve-fitting is never a unique solution, there was a considerable amount of ambiguity with regard to the existence of this feature. In fact, it could be shown that it was possible to fit the same spectrum without the β-peak, simply by varying the slope of the exponential tail on the graphitic peak. However, the use of monochromatic X-radiation allows for such improved resolution that the β-peak can now be seen as a distinctly resolved feature to the higher binding energy end of the main peak. The curve-fitting of these spectra could then be performed with a greater degree of confidence. This is particularly significant since increased confidence allows us to make more definite chemical predictions with regard to the changes on the surface of the fiber.[24]

Electrochemical oxidation produces an increase in the intensity of the oxide peak (peak 3 in Table 1) which corresponds to the bridged structure, the presence of which has been reported earlier.[12,18,20] The intensity of the bridged structure increases steadily as the level of oxidation is increased. However, at 0.75 A and above (samples (d) and (e)), there is not much of an increase in the level of oxidation, indicating that the surface of the fiber becomes oxide-saturated

at about 0.5 A. The relative percentages of carbon and oxide present are shown in table 5 and

table 6, for the monochromatic and achromic experiments respectively.

Tables 5 and 6 show that the β-peak (peak 2) increases in intensity as the amount of

oxidation increases. Thus in *a* it is only about 4% (total oxide peaks (2-6) 15%) but rises to

about 16-17% in *b and c* (total oxide peaks (2-6) around 32%) and to about 20-30% in *d* and

e (total oxide peaks around 33%).   Thus the relative intensity of the β-peak increases as the

amount of oxide increases.

There is an abnormal increase in both graphitic (peak 1) and oxide character (all forms of

oxidized carbon - peaks 2 to 6) at and above 0.75 A in the case of the achromatic experiment.

This is a result of the decomposition of the fiber surface by exposure to X-rays in the

spectrometer.[18] This behavior is not seen in the case of the monochromatic experiment. This

is because the monochromator reduces, or eliminates sources of potential sample decomposition:

(i) It increases the effective distance between the source and sample from about 1mm to about

1.4 meters almost eliminating the chance of heat from the X-ray target reaching the sample

surface.   Heat from the gun is probably the principal cause of sample damage.

(ii) It eliminates Bremstraahlung radiation which might cause sample decomposition.

(iii) It uses a monochromator which does not use a window for these experiments, so eliminating

electrons produced in the window reaching the sample surface and causing decomposition.

As a result, the amount of decomposition produced by exposure to X-radiation is minimal.

Significant increases in the intensity of the other functionalities are not seen as the level

of oxidation is increased. A slight increase in the oxide (peak 4) is seen at oxidation levels

higher than 0.5 A. This probably corresponds to the formation of small amounts of iron and

chromium oxides. Again, this is due to the contamination of the fiber from the stainless steel

rollers. Although this is an unintentional contamination, it is possible to use the presence of these contaminants as markers to monitor changes in the fiber-matrix interface during composite manufacture.

O1s Spectra. The O1s spectra are shown in figure 5(i) and figure 5(ii). The spectra were fitted to two component peaks. The fiber (a) shows a peak of weak intensity at 534 eV, which is as expected for untreated fibers.[25] The oxidized fibers ((b) - (e)) show intense O1s peaks at 534 eV and a less intense shoulder at about 531 eV, the intensity of which increases as the level of oxidation increases. The peak at 534 eV corresponds to the bridged structure which is the dominant oxide feature in the C1s region as well. The peak at 531 eV corresponds to hydroxide functionality in a metal (rather than carbon) hydroxide. The level of oxidation indicated by the C/O ratio is lower when the 531 eV peak is present, even though the chemically shifted peaks in the C1s region would not suggest such a low C/O ratio. This indicates that the oxygen is not associated with carbon, further supporting the assignment of the 531eV peak to metal hydroxide functionality. We can thus conclude that this feature arises from the formation of the hydroxides of iron and chromium, due to the contamination of the surface of the fiber from the stainless steel rollers used in the pilot plant. No significant differences in the spectra collected using monochromatic and achromic radiation are observed. For the untreated fiber in (a), the increased resolution achievable with the narrow radiation from the monochromator allows two peaks to be resolved out, whereas the corresponding achromic spectrum shows only a single broad feature. This again demonstrates that the narrower linewidth X-radiation provided by the use of a monochromator allows additional chemical information to be provided.

Valence Band Spectra   Figures 6(i) and 6(ii) show the valence band spectra for the untreated and electrochemically oxidized fiber samples. It has been reported in the past that information not available from the core region can be obtained by a detailed analysis of the valence band region.[26,28] The valence band probes more deeply into the sample and consequently, significant differences in the surface sensitivity between achromic and monochromatic radiation are not observed in this region, since the oxidized species are found in the outer surface region.

The untreated fiber (a) shows an intense C2s feature at about 20 eV corresponding to the presence of a sample that is predominantly carbon. The corresponding achromic spectrum shows an intense C2s feature and a much weaker O2s signal at about 25 eV. As the fiber is oxidized (samples (b) - (e)), the O2s peak becomes steadily more intense. There is a simultaneous decrease in the intensity of the C2s peak as oxidation proceeds. At higher oxidation levels ((d) and (e)), a new feature at about 5 eV is seen. This corresponds to an oxide of iron, as a consequence of contamination from the steel rollers. This feature is seen in both the achromic and monochromatic case. The monochromatic spectra are better resolved and this feature can be seen to consist of three components. From previous work, this has been found to be Fe_2O_3.[29] In addition, an intense peak at 45 eV (not shown) would also be seen, corresponding to the formation of Cr_2O_3, also a result of contamination from the stainless steel rollers. Changes in the shape of the O2s peak may also correspond to the formation of these metal oxides.

In general, the spectra obtained in the valence band region, both with monochromatic and achromic radiation, are characteristic of carbon fibers oxidized in acidic media.[28] The formation of the bridged structure as the predominant oxide species is also confirmed by comparison with our previous work. [12,18]

24

CONCLUSIONS

It has been found that the use of monochromatic X-radiation significantly reduces the decomposition of carbon fibers that normally occurs as a result of exposure to X-rays during XPS analysis. Monochromatic radiation leads to a substantial reduction in the fwhm of the C1s graphitic peak and in C1s peaks from oxidized carbon. This narrowing results in improved resolution so that previously unresolved features can be seen. In particular the presence and importance of the β- peak in the fitting of the C1s region is established.

This study shows that the chemical changes introduced on the surface of a fiber can be studied more effectively by using monochromatic X-radiation while simultaneously eliminating some of the decomposition problems encountered during analysis using achromatic radiation.

25

REFERENCES

1. R. Bacon, *J. Appl. Phys.* 31, 284 (1960).

2. R. Bacon and M. M. Tang, *Carbon* 2, 227 (1964).

3. A. Shindo, *J. Ceram. Assoc. Jpn.* 69, 195 (1961); A. Shindo, *Carbon* 1, 391 (1964).

4. W. Watt, L. N. Philipps and W. Johnson, *Engineer* 221, 815 (1966).

5. A. Proctor and P.M.A. Sherwood, *J. Electron Spectrosc. Relat. Phenom.* 27, 39 (1982).

6. P.M.A. Sherwood, *Mater. Res. Soc. Proc.* 270, 79 (1992).

7. Y. Xie and P. M. A. Sherwood, *Appl. Spectrosc.* 43, 1153 (1989).

8. C. Kozlowski and P. M. A. Sherwood. *J. Chem. Soc., Faraday Trans. 1* 80, 2099 (1984).

9. T. Wang and P. M. A. Sherwood, *Chem. Mater.* 6, 788 (1994).

10. Y. Xie and P. M. A. Sherwood, *Chem. Mater.* 6, 650 (1994).

11. A. Proctor and P. M. A. Sherwood, *Carbon* 21, 53 (1983).

12. C. Kozlowski and P. M. A. Sherwood, *J. Chem. Soc., Faraday Trans 1* 81, 2745 (1985).

13. C. Kozlowski and P. M. A. Sherwood, *Carbon* 24, 357 (1986).

14. C. Kozlowski and P. M. A. Sherwood, *Carbon* 25, 751 (1987).

15. C. L. Weitzsacker, M. Bellamy and P. M. A. Sherwood, *J. Vac. Sci. Technol. A* 12, 2392 (1994).

16. C. L. Weitzsacker and P. M. A. Sherwood, *Surf. Interface Anal.* 23, 531 (1995).

17. Y. Xie and P. M. A. Sherwood, *Appl. Spectrosc.* 44, 797 (1990).

18. Y. Xie and P. M. A. Sherwood, *Appl. Spectrosc.* 44, 1621 (1990).

19. J. Harvey, C. Kozlowski and P. M. A. Sherwood. *J. Mater. Sci.* 22, 1585 (1987).

20. Y. Xie and P. M. A. Sherwood, *Chem. Mater.* 2, 293 (1990).

21. P.M.A. Sherwood, *J. Electron Spectrosc. Relat. Phenom.* XX, xx (1996)

22. Y. Xie and P. M. A. Sherwood, *Appl. Spectrosc.* 45, 1158 (1991).

23. P. M. A.Sherwood, in *Practical Surface Analysis in XPS and AES in Practical Electron*

Spectroscopy, ed. by D. Briggs and M. P. Seah, Appendix 3, pp. 555-586. Wiley, Chichester (1990).

24. P. M. A. Sherwood, chapter on "Composites" in *Problem-Solving Methods in Surface Analysis*, ed. by J.C. Rivière and S. Myhra, Marcel Dekker, Inc. in press.

25. Y. Xie, T. Wang, M. A. Rooke and P. M. A. Sherwood, *Surf. Sci. Spectrosc.* 1, 210 (1992).

26. Y. Xie and P. M. A. Sherwood, *Chem. Mater.* 1, 427 (1989).

27. S. Thomas and P. M. A. Sherwood, *Anal. Chem.* 64, 2488 (1992).

28. Y. Xie and P. M. A. Sherwood, *Chem. Mater.* 3, 164 (1991).

29. S. Thomas and P. M. A. Sherwood, *Surf. Interface Anal.* 20, 595 (1993).

30. J. H. Schofield. *J. Electron Spectrosc. Relat. Phenom.* 8, 129 (1976).

31. M. P. Seah and W. A. Dench, *Surf. Interface Anal.* 1, 2 (1979).

32. Annual Book of ASTM Standards, *Surf. Interface Anal.* 17, 889 (1991).

33. A Proctor and P. M. A. Sherwood, *Anal. Chem.* 54, 13 (1982).

Table 1.	Description of Samples Studied	

Designation	Description of electrochemical treatment
a	Untreated (as received), rinsed in distilled water
b	0.25 A / 1 M HNO_3, rinsed
c	0.50 A / 1 M HNO_3, rinsed
d	0.75 A / 1 M HNO_3, rinsed
e	1.00 A / 1 M HNO_3, rinsed

Table 2.	Description of Material Studied

Designation	Description of material type
a	Highly Ordered Pyrolytic Graphite (HOPG)
b	Pitch-based E120 Carbon Fiber
c	PAN-based Type II Carbon Fiber

Table 3.	Approximate Atomic Ratios	

Experiment	Monochromatic C1s/O1s	Achromic C1s/O1s
a	7.2	4.1
b	3.1	3.9
c	3.2	3.0
d	3.0	2.7
e	1.1	1.6

Table 4.	Component Peak Positions used for C1s fits	

Peak Number	Functionality	Binding Energy (eV)
1	Graphitic carbon	284.6
2	Beta Carbon	285.3
3	Bridged structure	286.8
4	C = O	288.2
5	COOH, COOR	289.0
6	π- π* shake-up	290.7
7	Plasmon	291.5

Table 5.	Relative Areas obtained from C1s fitted Spectra					
Experiment	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6
a	81.3 %	3.67 %	4.72 %	2.99 %	4.19 %	3.14 %
uncertainty*	0.028	---	0.360	0.350	0.024	0.009
b	50.8 %	15.7 %	26.3 %	5.30 %	0.29 %	1.54 %
uncertainty	0.009	---	0.007	0.005	0.007	0.005
c	52.2 %	16.9 %	27.2 %	3.32 %	0.13 %	0.14 %
uncertainty	---	---	0.011	0.006	0.005	0.003
d	37.2 %	29.3 %	26.9 %	5.31 %	0.63 %	0.63 %
uncertainty	---	---	0.010	0.008	0.004	0.004
e	45.1 %	21.7 %	25.5 %	5.10 %	1.09 %	1.53 %
uncertainty	---	---	---	---	0.009	0.008

* Values represent 95% confidence limits (two standard deviations for the fitted areas) for the peak area

Table 6.	Relative Areas obtained from C1s fitted Spectra					
Experiment	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6
a	72.3 %	10.3 %	8.59 %	4.09 %	4.41 %	0.27 %
uncertainty*	0.030	---	---	0.062	0.530	0.007
b	47.8 %	16.4 %	30.7 %	3.01 %	1.05 %	1.05 %
uncertainty	---	---	---	0.100	0.110	0.100
c	41.2 %	20.5 %	27.2 %	8.33 %	1.29 %	1.21 %
uncertainty	---	---	---	0.17	0.034	0.012
d	47.1 %	21.6 %	20.8 %	8.97 %	0.82 %	0.69 %
uncertainty	---	---	---	0.021	0.016	0.014
e	48.8 %	18.2 %	22.8 %	5.70 %	2.38 %	2.15 %
uncertainty	---	---	---	---	0.013	0.012

* Values represent 95% confidence limits for the peak area.
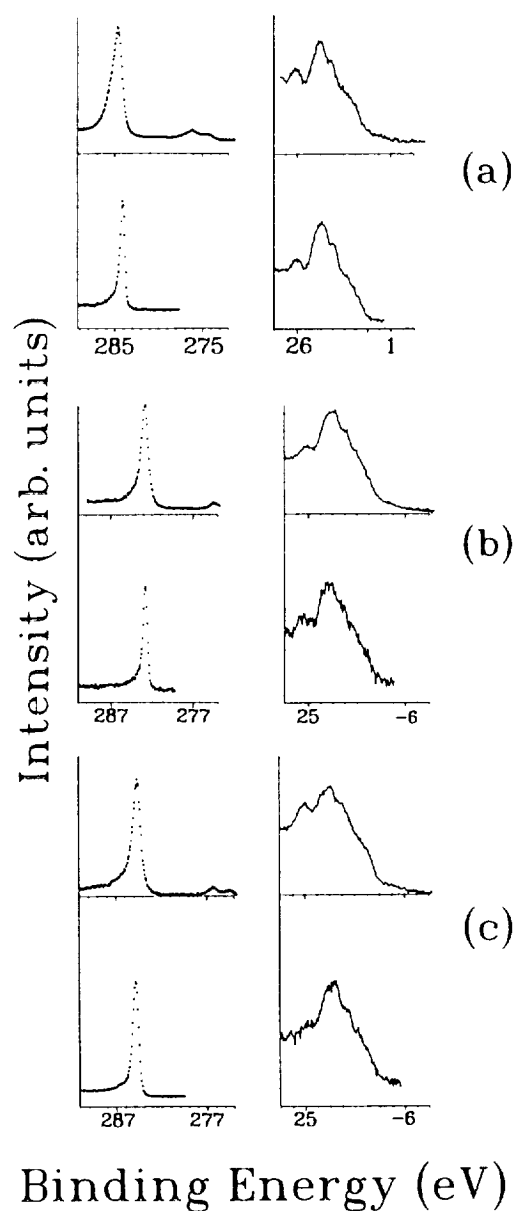
Figure 1 C1s XPS spectra (left side) for various graphitic materials using monochromatic and achromic x-radiation. (a) highly ordered pyrolytic graphite (b) E-120 pitch-based carbon fiber and (c) PAN-based Type II carbon fiber.

Valence band XPS spectra (right side) for various graphitic materials using monochromatic and achromic x-radiation. (a) highly ordered pyrolytic graphite (b) E-120 pitch-based carbon fiber and (c) PAN-based Type II carbon fiber

31
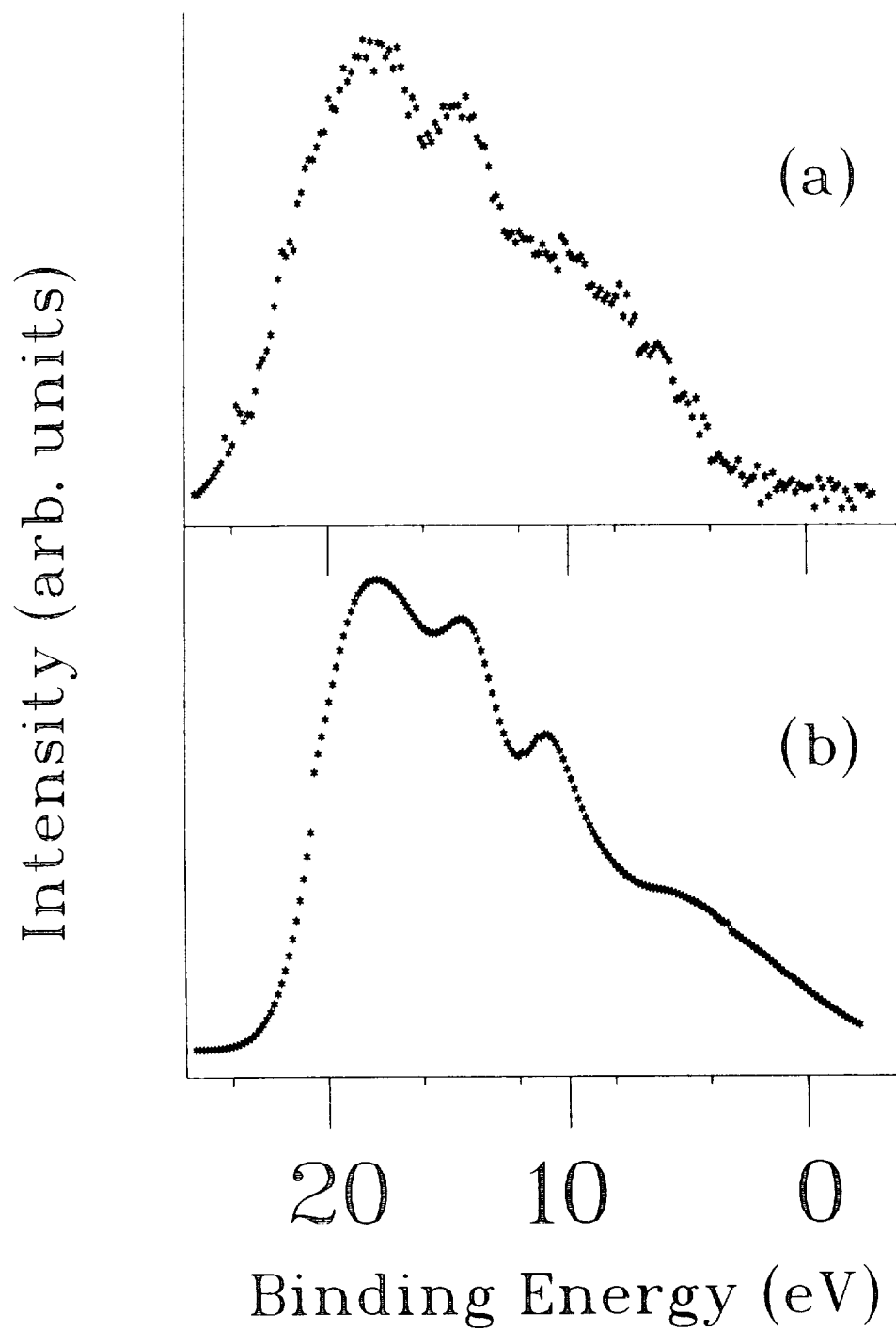
Figure 2 Comparison of HOPG valence band XPS spectra obtained (a) experimentally using AlKα monochromatic radiation and (b) calculated using a band structure calculation for a two-dimensional graphite lattice.
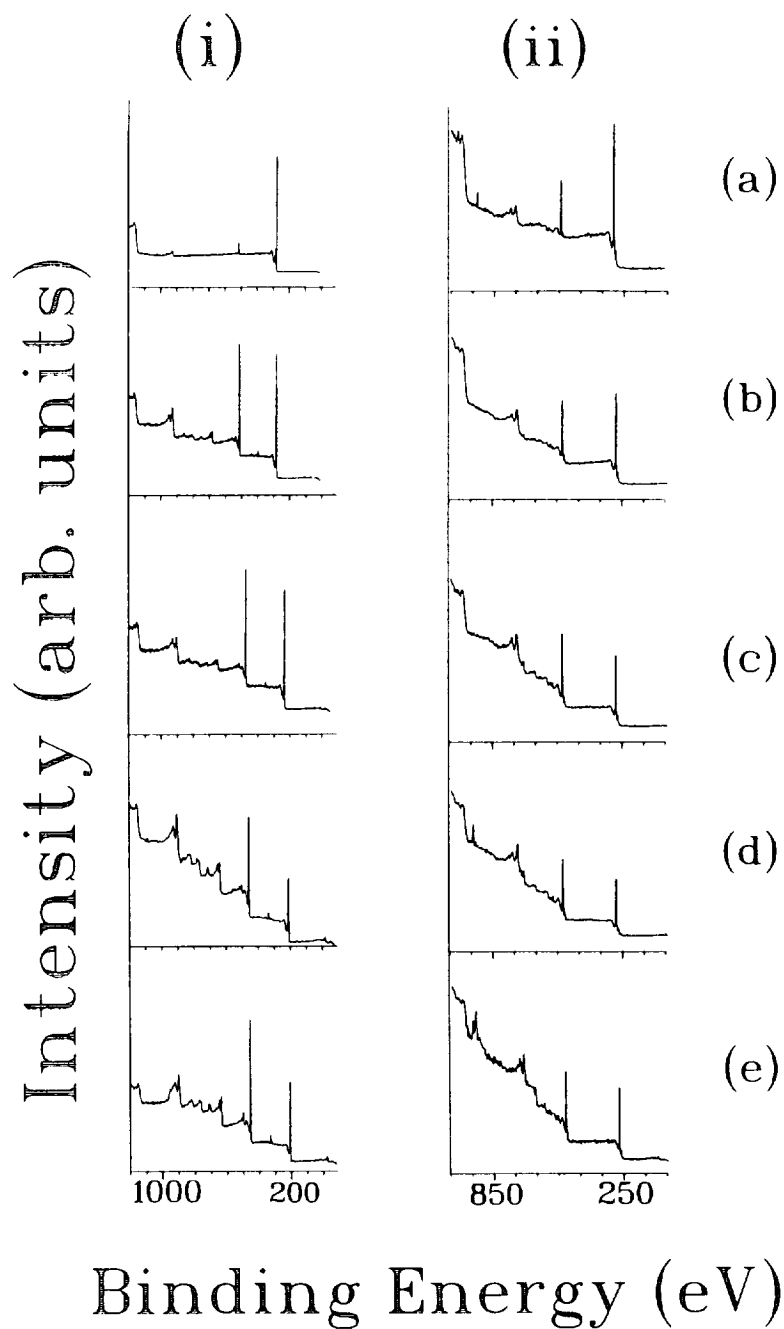
Figure 3 Overall XPS spectra collected using monochromatic x-radiation (i) for (a) untreated M40 carbon fiber; (b - e) for fibers electrochemically oxidized in 1M HNO₃ solution for 40s at currents ranging from 0.25 A to 1.00 A.

Overall XPS spectra collected using achromic x-radiation (ii) for (a) untreated M40 carbon fiber; (b - e) for fibers electrochemically oxidized in 1M HNO₃ solution for 40s at currents ranging from 0.25 A to 1.00 A.

33
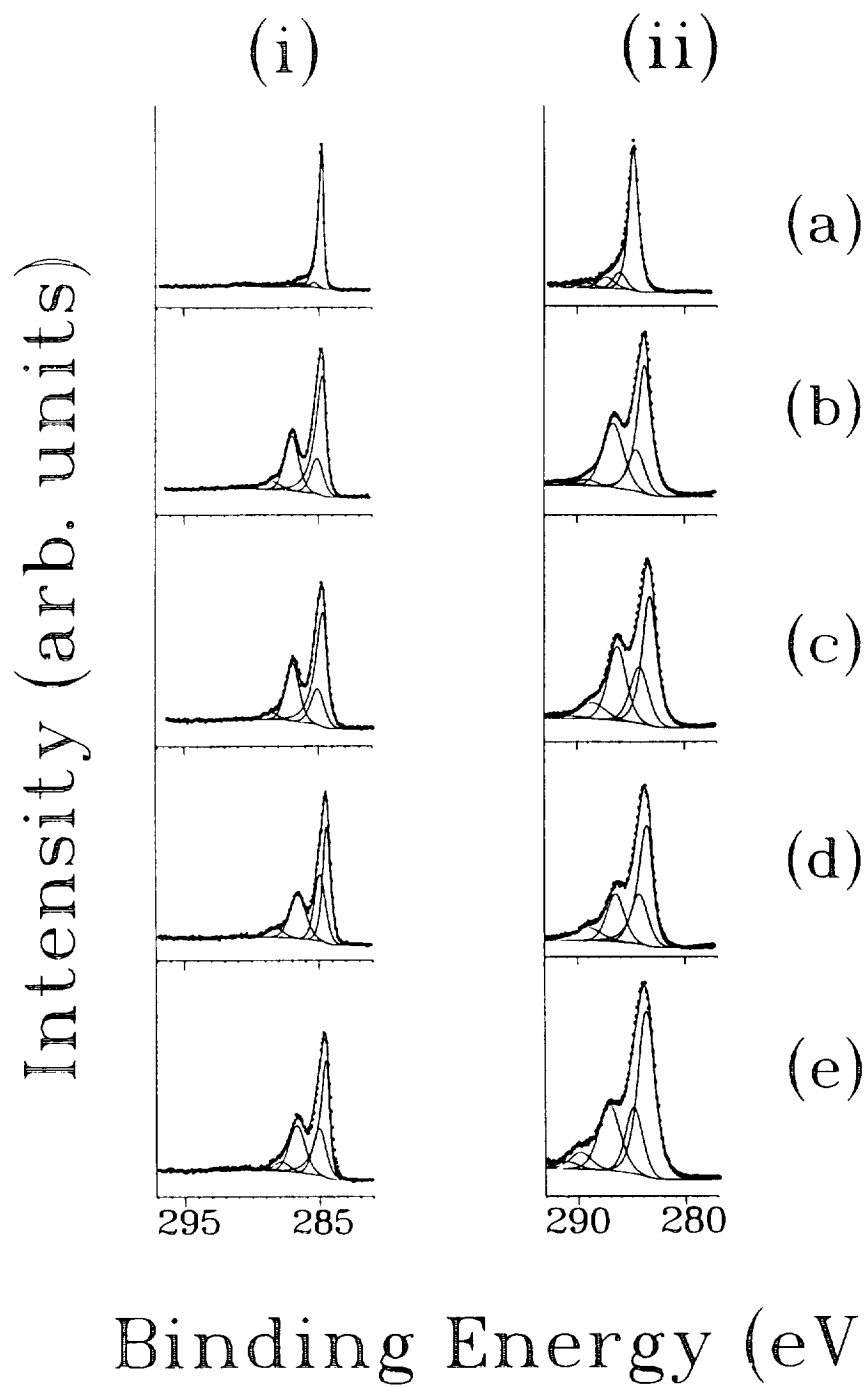
Figure 4 Curve-fitted C1s spectra for untreated M40 carbon fibers using (i) monochromatic x-radiation and (ii) achromic x-radiation.
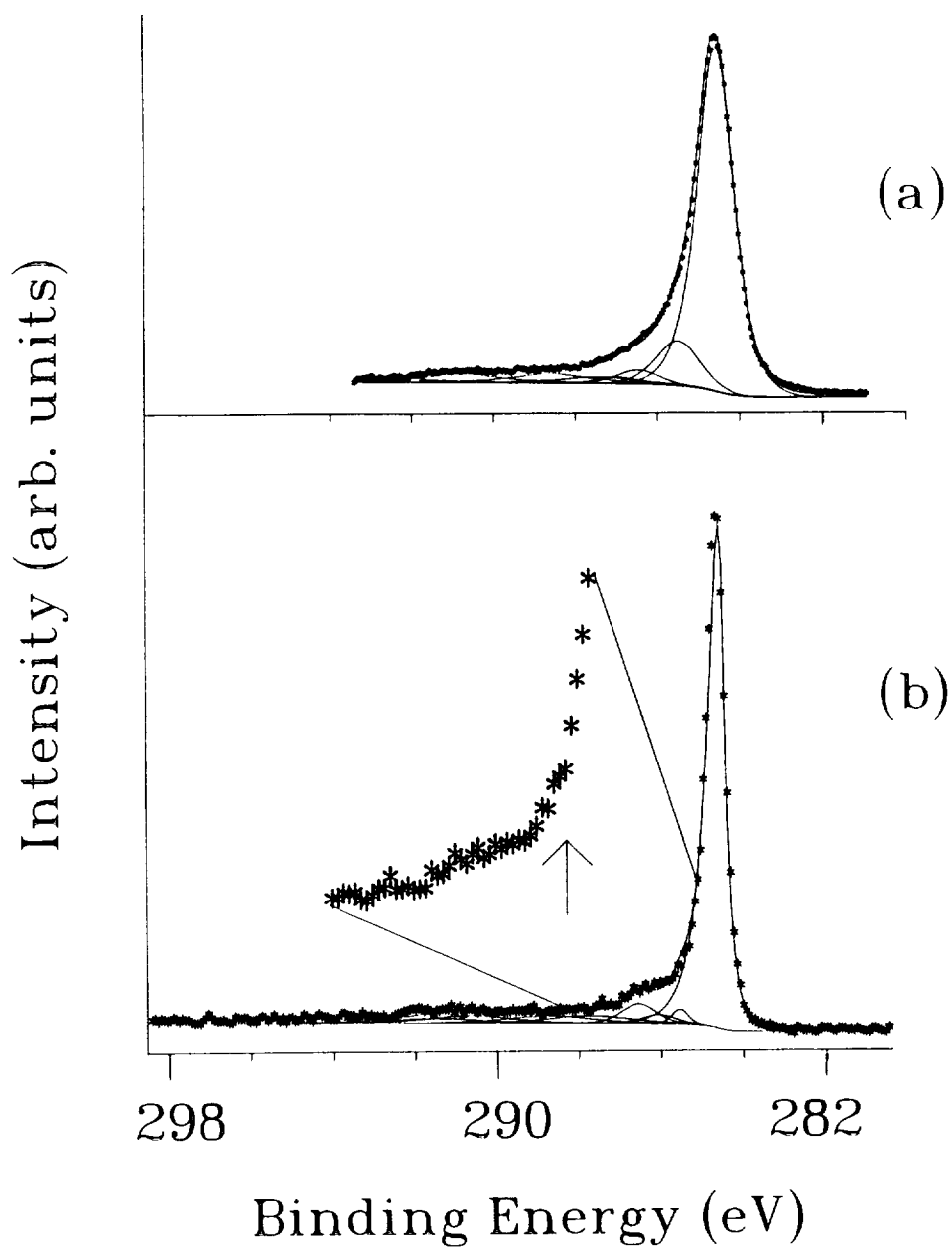
Figure 5 Curve-fitted C1s spectra (left) collected using monochromatic Al Kα x-radiation for (a) untreated (as received) M40 carbon fiber; (b - e) for fibers electrochemically oxidized in 1M HNO₃ for 40s at currents ranging from 0.25 A to 1.00 A.

Curve-fitted C1s spectra (right) collected using achromatic Mg Kα x-radiation for (a) untreated (as received) M40 carbon fiber; (b - e) for fibers electrochemically oxidized in 1M HNO₃ for 40s at currents ranging from 0.25 A to 1.00 A.
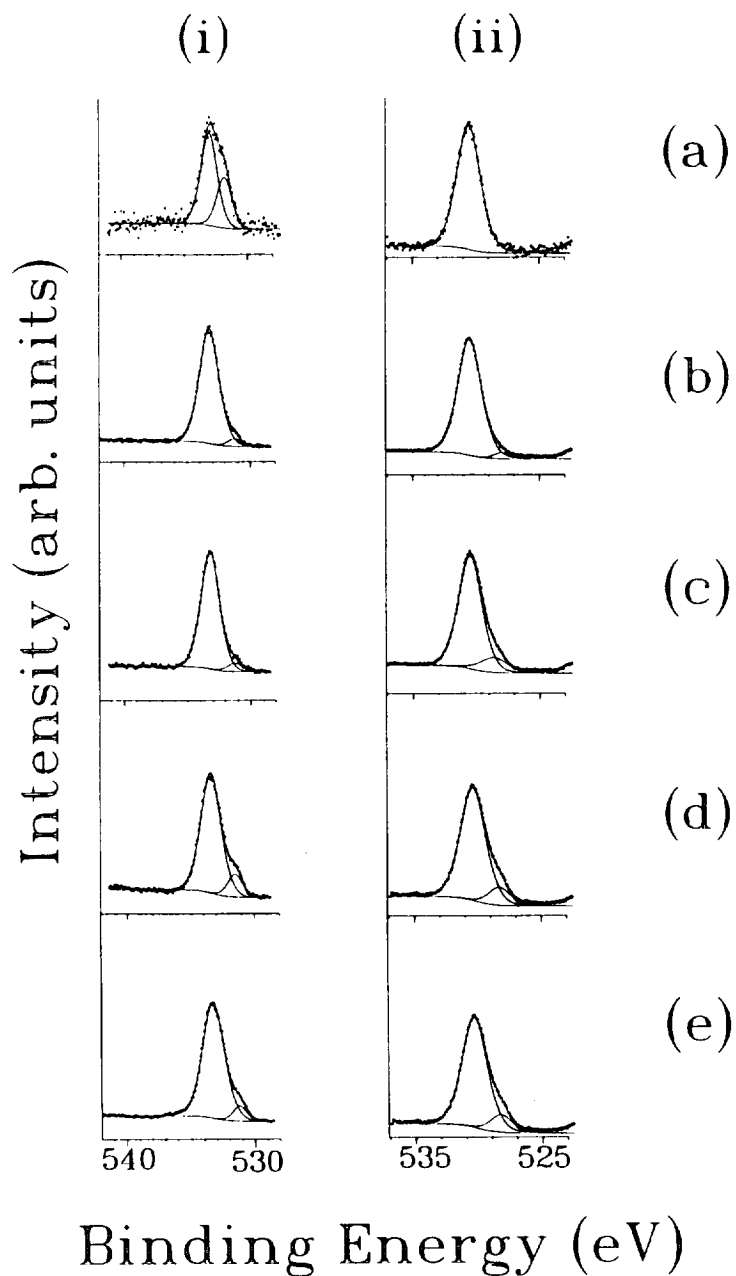
Figure 6   Curve-fitted O1s spectra (i) collected using monochromatic Al Kα x-radiation for (a) untreated M40 carbon fiber; (b - e) for fibers electrochemically oxidized in 1M HNO_3 for 40s at currents ranging from 0.25 A to 1.00 A.

Curve-fitted O1s spectra (ii) collected using achromic Mg Kα x-radiation for (a) untreated M40 carbon fiber; (b - e) for fibers electrochemically oxidized in 1M HNO_3 for 40s at currents ranging from 0.25 A to 1.00 A.
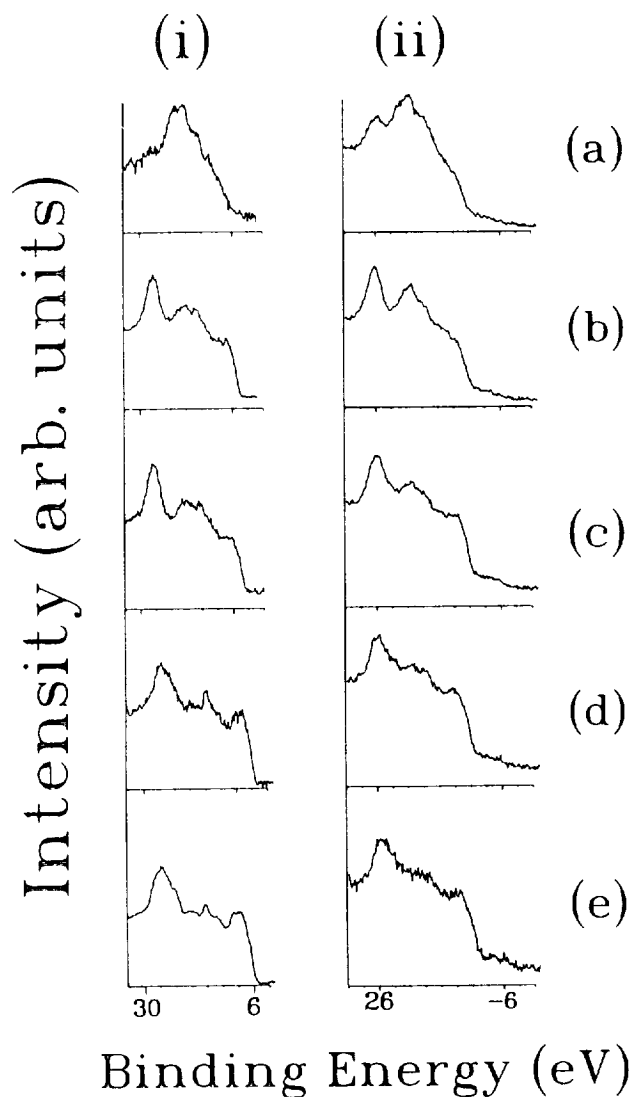
Figure 7   Valence Band spectra collected (i) using monochromatic Al Kα x-radiation for (a) untreated M40 carbon fiber; (b - e) for fibers electrochemically oxidized in 1M HNO₃ for 40s at currents ranging from 0.25 A to 1.00 A.

Valence Band spectra collected (ii) using achromic Mg Kα x-radiation for (a) untreated M40 carbon fiber; (b -e) for fibers electrochemically oxidized in 1M HNO₃ for 40s at currents ranging from 0.25 A to 1.00 A.

37

An XPS Study of the Interfacial Interaction of a Polyimid Resin with Surface Treated PAN-based Carbon Fibers

M.A. Rooke, H. Viswanathan, N. Havercroft and Peter M.A. Sherwood

(Report of work to be submitted as a paper - Reported in Chapter 9, Ph.D. thesis of M.A. Rooke 1996)

Abstract

This work reports a study of the interfacial chemistry of M40 PAN based carbon fibers with a new thermoplastic polyimid resin from Du Pont, known as Avimid® K3B. This resin is thought to offer potentially superior chemical and mechanical properties for the development of carbon-plastic composites with improved mechanical performance and desirable thermal tolerance. X-ray photoelectron spectroscopy (XPS) results are included of the electrochemical oxidation of the M40 fiber prior to coating with K3B. The interfacial interaction of the K3B with the fiber was investigated with valence band photoemission, by applying a thin film of the coating onto the oxidized carbon fiber surface and the changes in the valence band spectra monitored.

Topographical changes in the fiber surface during electrochemical treatment are reported using atomic force microscopy (AFM).

Introduction

Development of lightweight composite materials using carbon-plastic composites has become an active area of materials research, by combining the mechanical strength of carbon fibers with the superior fracture resistance and toughness of thermoplastic polymers. The aim of this study is to develop an improved adhesion between the carbon fiber and a new polymer matrix, polyimid K3B. This type of carbon-plastic composite has important applications in the development of the High Speed Civil Transport (HSCT) currently of interest to NASA. Surface treatment of the carbon fibers was found to lead to a substantial improvement in the composite mechanical properties.[1-13] Studies carried out by Wang and Sherwood[14-16] have concentrated on improving the fiber-matrix interfacial adhesion, particularly the chemical interaction of the surface groups on the fiber with functional groups on the resin. By surface treating the carbon fibers, the desired type of functionality can be introduced onto the fiber, which when combined with the resin will allow chemical reaction to occur at the interface, and therefore crosslinking the resin molecules to the fiber. In some cases it was found necessary to introduce coupling agents, short polymer molecules which had the necessary functional groups on the ends of the molecule to attach to both resin and fiber.

In this study a PAN based carbon fiber known as M40 was to be treated and combined with the K3B resin, which would act as the matrix in the carbon-plastic composite. The interface between the fiber and the K3B resin was analyzed with X-ray photoelectron spectroscopy (XPS) to determine whether chemical interaction could be induced by surface treating the carbon fibers in nitric acid prior to application of the K3B resin. Nitric acid has previously been reported[14-19]

39

to produce hydroxyl, carbonyl and a keto-enol bridged functionality on PAN based carbon fiber surfaces when electrochemically treated. The distribution of the hydroxyl or bridged structure (keto-enol form) is found to be dependant upon the electrode potential used during the anodic treatment of the carbon fibers. Below 2.0V the most abundant functional group was found to be hydroxyl (C-OH), and at potentials above this the functionality changed to predominantly carbonyl groups (C=O). Eventually, if the treatment is maintained for sufficient time there will be as many carbonyl groups as hydroxy groups and a situation will develop where the predominant functionality is a *bridged* structure, consisting of a keto-enol tautomerism, with the proton of the hydroxyl group shifting between the hydroxyl group to the carbonyl group in a stable resonance form.

Experimental

The carbon fiber used in this study was an M40 PAN based fiber manufactured by Du Pont which contained no sizing material. Fibers were wrapped after treatment into a double tow of approx. 6000 fibers using aluminum foil at both ends to secure the fibers for AFM and XPS analysis. Galvanostatic electrochemical treatment was carried out on purpose-made treatment line (see fig. 4.1), with the tow of fibers being pulled through two washing baths before and after electrochemical treatment. The current was maintained using a Ministat Research Potentiostat (model 402R), manufactured by Thompson Electrochem Ltd. The fiber passed through the electrolyte using conducting stainless steel rollers, which acted as the working electrode. Two graphite rods were placed in close proximity to the fibers and were connected to the potentiostat to act as the counter electrode. After being oxidized the fibers were washed and passed into a heated drying box before being collected at the end of the treatment line.

Application of K3B resin to the carbon fibers was done by dipping the tow of fibers into

a 1% solution of K3B resin in 1-methyl-2-pyrrolidinone, which was prepared by simply heating

the solvent until a saturated solution was produced. The solubility of K3B in this solvent is low,

although this is one of the few solvents which will dissolve K3B. Prior to application of the

resin, the fibers had been anodically oxidized at 0.50 A using the treatment line and dried to

remove the water. The fibers were then dipped into the solution for 5 minutes, removed and dried

in a convection oven at 70°C for 1 hour. Coating of the copper plate used to obtain a spectrum

of K3B alone was done in the same manner.

The XPS data was collected on a VSW HA150 X-ray photoelectron spectrometer using

monochromatic Al Kα radiation (300W), produced using a VSW 32 quartz crystal

monochromator. Photoelectrons were detected using a 16 channel multichannel detection system.

Use of the monochromatic radiation with a multichannel analyzer enabled collection of data from

the carbon fibers without causing significant degradation to the functional groups present. Earlier

samples when analyzed using conventional XPS were found to degrade rapidly producing

unsatisfactory data. Both instruments were calibrated with copper[28] and a base pressure of around

10^{-9} Torr for all experiments. Curve fitting of the XPS core levels was carried out with a non-

linear least squares curve fitting program with a Gaussian-Lorentzian product function,[30] with a

non-linear background included in the fit.[31] The Gaussian-Lorentzian mix was taken as 0.5,

except for the 'graphitic' carbon peak, which was taken as 0.8 with an exponential tail. The

binding energy of the most intense peak in the C1s spectra was taken as 284.6 eV for calibration

purposes.

Atomic force microscopy (AFM) was carried out on a Wyko SPM 30 microscope. The

carbon fiber samples were mounted onto double sided tape and held firmly with colloidal

graphite paint. The probe tips were scanned laterally across the fibers using a scan speed of approx. 1 Hz and a tip force of 30-50 nN.

Results & Discussion

Electrochemical oxidation of the carbon fibers

The initial experiment was designed to use monochromatic radiation to analyze the surface of the fiber after electrochemical treatment without causing degradation of the fibers, previously found when run on a conventional XPS instrument. No degradation was found to occur using the VSW HA150. The curve-fitted XPS core spectra are shown in fig. 9.1. The top row shows the untreated M40 fiber with a very narrow graphitic C1s peak for the fiber surface. The full width at half maximum for this peak is found to be 0.56 eV. This shows conclusively that there is almost no functionality on the fiber surface prior to treatment, as was expected. The overall spectrum for the untreated fiber shows a small O1s peak, which is also shown as a separate core level. The valence band is characteristic of a carbon fiber, showing strong features due to primarily C2s and C2p bonding orbitals. The 0.250 A treated sample shows a shoulder on the C1s peak chemically shifted from the main graphitic peak by approximately 2 eV. This shift is consistent with a *bridged* type functionality developing on the fiber surface. The intensity of the O1s peak has grown considerably in both the core and overall spectra, steadily increasing in intensity as the applied current is increased. If one looks carefully at the overall spectra for all three of the treatment times, a peak can be clearly seen to develop at a binding energy of approximately 400 eV. This is due to nitrogen functionality on the fiber surface, caused by the anodic oxidation of the carbon fibers. The intensity of the N1s does not appear to change over

this range of applied current.

Table 1 C1s peak shifts, relative areas and atomic ratios.

Sample	Peak 1 B.E. Area (eV) (%)	Peak 2 C.S. Area (eV) (%)	Peak 3 C.S. Area (eV) (%)	Peak 4 C.S. Area (eV) (%)	C1s/O1s Peak Area (%)	C/O ratio[a] (%)
0.00 A	284.6 68.5	1.3 19.8	4.7 5.9	7.2 5.8	7.329	22.23
0.25 A	284.6 58.0	1.3 11.2	2.5 24.6	4.0 6.1	0.987	2.996
0.50 A	284.6 43.0	0.6 21.7	2.3 28.4	3.9 6.8	0.875	2.688
0.75 A	284.6 51.7	0.8 19.0	2.4 19.8	4.0 9.4	0.716	2.172

a Approx. Atomic amount
Note: Inelastic mean free paths used in the At. amount ratio were calculated using Seah & Dench equations [M.P. Seah and W.A. Dench, *Surf. Interface Anal.*, 1, 2 (1979).]

Table 2 Peak positions and relative areas for the O1s and N1s spectra.

Sample	Peak 1 (O1s) B.E. (eV)	Area (%)	Peak 2 (O1s) B.E. (eV)	Area (%)	Peak 1 (N1s) B.E. (eV)	Area (%)	Peak 2 (N1s) B.E. (eV)	Area (%)
0.00 A	533.7	66.8	532.5	33.2				
0.25 A	533.1	95.7	531.0	4.3				
0.50 A	532.9	93.9	530.7	6.9				
0.75 A	532.9	87.7	530.7	12.3	407.3	100	-	-
K3B/Cu	532.7	72.1	530.5	27.9	400.7	51.6	399.0	48.4
K3B/fiber	532.5	100	-	-	402.1	8.8	400.8	91.2

The approximate C/O atomic ratios and chemical shifts for the C1s spectra are shown in table 1, and the peak areas and positions for the O1s and N1s spectra are shown in table 2. These ratios show a large C/O ratio for the untreated M40 fiber, as would be expected, which decreases rapidly with oxidation on the treatment line. The type of oxygen functionality produced during surface treatment remains constant, with just the ratio of C/O decreasing, suggesting that the concentration of the keto-enol bridge structure increases steadily with applied current.

A number of interesting features can be seen developing in the overall and valence spectra

with increasing anodic current in fig. 1. The overall spectra show the growth of peaks at binding energies of between 500 eV and 800 eV, steadily growing with increasing current. These peaks are due to chromium ions, deposited onto the fibers during electrochemical treatment. The rollers used to supply the fiber tow with current are made of stainless steel, which is known to be high in chromium content near the surface. It is believed that this chromium leaches out and becomes bonded to the fibers during electrochemical treatment. The overall spectrum after 0.750A treatment clearly shows peaks due to Cr2s and Cr2p at 700 eV and 575 eV binding energy respectively. The valence band also shows the presence of chromium ions with a narrow peak, steadily increasing in intensity with current at a binding energy of approximately 45 eV. The sudden increase in intensity at 0.750 A suggests that the chromium is leached from the stainless steel much more readily at higher applied currents. A shoulder found at lower binding energy than the main peak on the O1s is due to oxygen in chromium oxide.

The presence of chromium was unintentional, although it will be seen as a useful *marker* peak in the experiment described below. The chromium was known to be present only on the surface of the electrochemically treated carbon fibers, and as such, the presence of this peak in the valence spectra would suggest that photoelectrons were able to be detected from the resin-fiber interface.

Analysis of the fiber-matrix interface

The fiber-matrix interface is a buried interface. We have taken an approach where such interfaces can be examined by setting up a situation where the buried interface is close to the surface and so comes within the probe depth of valence band photoemission. The approach involves preparing the buried interface by placing a very thin film of the matrix material onto

the surface of a fiber.   This can be done by immersing the fiber into a solution of the matrix material, and then allowing the solvent to evaporate.   The spectrum of the interface can be obtained by obtaining the following spectra:

(i) Spectrum of Matrix Alone = M

(ii) Spectrum of Fiber Surface Alone = F

(iii) Spectrum of the fiber coated with a very thin layer of matrix material = S. One must ensure that the spectrum of the underlying fiber can be seen in the XPS data, so that the buried interface is being probed.

The situation can be illustrated schematically:

Vacuum

_____

Matrix

_____

Buried Interface

_____

Fiber

If there is NO interaction at Fiber/Matrix interface

$$S = M + F$$

If there is CHEMICAL INTERACTION at Fiber/Matrix Interface

$$S =/= M + F$$

The spectrum of the interface region can be obtained by a difference spectrum (34) between M and F.

The XPS spectra of the oxidized carbon fibers, the K3B resin run as a powder and the resin coated fibers are all shown in fig. 2. Our earlier work has shown that the surface treatment used gives oxidized fibers that contain mostly *bridged* functionality. Fig. 2(a) shows the bridged functionality as the higher binding energy peak in the C1s region and the single peak in the O1s region. Figure 2 (c) shows the K3B resin coated fiber core level spectra. The C1s region shows the graphitic peak from the carbon fiber substrate together with a broad higher binding energy peak that appear different in width an intensity from the bridged functionality peak in Fig. 2(a). The O1s shows a broader peak than was seen for the substrate fiber. The surface treated fiber shows a low intensity N1s peak corresponding to some adsorbed nitrate ions from the nitric acid solution used for the electrochemical oxidation. In contrast the N1s region for the K3B coated fiber and that for K3B show a much more intense N1s feature. There is a significant change in the N1s binding energy on going from K3B to the carbon fiber coated with K3B providing strong evidence for chemical interaction between K3B and the fiber surface.

It is clear that the C1s spectrum for the K3B coated oxidized fiber cannot be constructed by the addition of the C1s spectrum of K3B and the C1s spectrum of the oxidized fiber. Thus $S =/= M + F$, and there is thus *evidence for chemical reaction between the oxidized fiber surface*

46

and the K3B.

The overall and valence spectra of the same three samples are shown in fig. 3. The valence band spectrum of the oxidized uncoated carbon fiber shows the intense peak due primarily to O2s bonding electrons, which would confirm the presence of a *bridged*-type functionality. The peak associated with chromium is also present at a binding energy of approximately 45 eV. This peak becomes important when looking at the valence spectrum in fig. 3(c). The presence of this peak can be used as a marker for the underlying fiber in the case of the coated fiber.

The K3B sample shows a spectrum with features that can be explained by an *ab initio* calculation on the repeat unit of the polymer shown in Fig. 4, which compares the experimental spectrum with a spectrum generated from the calculation. A proposed model structure[29] is shown in fig. 5. The exact structure of K3B is proprietary information and therefore has not been disclosed by Du Pont, the manufacturers of Avimid® K3B. The structure shown is a reasonable model for the repeat unit of the resin. It can be seen that the polymer has a distinct and characteristic valence band spectrum, and that the main features in the valence band spectrum can be explained by this model structure.

The interpretation of the valence band spectrum of the K3B coated oxidized carbon fiber shown in figure 3(c) can be explained by comparing the spectrum with that to the K3B and the oxidized fiber surface. The K3B coated oxidized carbon fiber has valence band features whose positions are similar to those in K3B alone and in the oxidized fiber alone, but the relative intensities of these features cannot be explained by any addition of K3B and the oxidized carbon

47

fiber spectrum.   It thus clear that again that S =/= M + F, and there is thus *complimentary*

evidence for chemical reaction between the oxidized fiber surface and the K3B.   Figure 6 shows

a schematic of the proposed interaction of K3B with an oxidized carbon fiber. The imide

functionality present in the K3B is thought to go through a ring-opening reaction producing a di-

amide, which then reacts with the carbonyl groups on the fiber. Hydrogen bonding between

hydroxyl groups on the fiber with amine groups on the resin might provide additional stability.

The structure would correspond to the solvent being involved in the chemical bonding process.

Further studies will be conducted to determine whether the reaction involves a direct reaction

with the resin, or a coupling reaction involving the solvent as a coupling agent as implied in

Figure 7.

Topographical analysis of oxidized carbon fibers

The effect of anodic treatment on the carbon fibers was investigated using atomic force

microscopy (AFM) on the carbon fibers at each level of treatment. The AFM images are shown

in both two dimensional and three dimensional form for treatments of 0.185-0.75 A in figs. 7-12

respectively.

The AFM images show not only the topographical changes of the carbon fibers but also

the statistical roughness increase calculated by the software used to run the instrument. The

roughness parameters are shown for each image, including the maximum height, minimum height,

range and root mean square roughness (RMS). Table 3 shows the RMS roughnesses of the three

levels of oxidation.

48

Table 3

Carbon fiber sample	RMS roughness (Å)
0.0185 A	1133
0.375 A	1500
0.750 A	2065

These results show that upon an increasing level of oxidation the carbon fibers undergo a paralleled degree of surface roughening which has been show to be the case by other researchers using both SEM, STM and AFM.[18-27]

Conclusions

Formation of carbonyl and hydroxyl functionality on PAN based carbon fibers has already been reported using a pilot plant treatment line by our group. The application of this technique to forming a carbon fiber-matrix resin interaction has been discussed in this report. It is clear than one can form a thin coating of polyimid K3B resin by dip coating a previously oxidized M40 carbon fiber. The results clearly show that an entire spool of the fiber can be readily oxidized with nitric acid and coated with a thin film of the K3B resin.

The XPS studies of the interface show that **chemical bonding is occurring between the oxidized carbon fiber and the K3B resin.** Surface roughening is found to occur on these fibers during oxidation, which would be expected to contribute to improved adhesion of the resin to the fiber.

References

1   F. Santiago, A.N. Mansour, R.N. Lee, *Surf. Interface Anal.*, **10**, 17 (1987)

2   L.T. Drzal, M.J. Rich, M.F. Koenig, P.F. Lloyd, *J. Adhesion*, **16**, 133 (1983)

3   A. Garton, J.H. Daly, W.T.K. Stevenson, D.M. Wiles, *J. Polym. Sci.* A: Poly.   Chem., **24**, 2383 (1986)

4   P.W.M. Peters, G.S. Springer, *J. Comp. Mater.*, **21**, 157 (1987)

5   H.L. Needles, K.W. Alger, R. Okamoto, *J. Reinforced Comp.*, **6**, 357 (1987)

6   J.D.H. Hughes, *Comp. Sci. Tech.*, **41**, 13 (1991)

7   W.D. Bascom, K.J. Yon, R.M. Jensen, L. Cordner, *J. Adhesion*, **34**, 79 (1991)

8   N. Sato, T. Kurauchi, *J. Mater. Sci. Lett.*, **11**, 362 (1992)

9   C.L. Weitzsacker, M. Bellamy, P.M.A. Sherwood, *J. Vac. Sci. Technol. A*, **12**,   4, 2392 (1994)

10   J.A. King, D.A. Buttry, D.F. Adams, *Poly. Comp.*, **14**, 4, 292 (1993)

11   J.A. King, D.A. Buttry, D.F. Adams, *Poly. Comp.*, **14**, 4, 301 (1993)

12   D.M. Blackletter, D. Upadhyaya, *Poly. Comp.*, **14**, 5, 430 (1993)

13   G. Krekel, K.J. Hüttinger, W.P. Hoffman, *J. Mat. Sci.*, **29**, 3461 (1994)

14   T. Wang, P.M.A. Sherwood, *Chem. Mater.*, **6**, 788 (1994)

15   T. Wang, P.M.A. Sherwood, *Chem. Mater.*, **7**, 1029 (1995)

16   T. Wang, P.M.A. Sherwood, *Chem. Mater.*, **7**, 1031 (1995)

17   C. Kozlowski, P.M.A. Sherwood, *J. Chem. Soc., Faraday Trans.* I, **80**, 2099   (1984)

18   C. Kozlowski, P.M.A. Sherwood, *Carbon*, **25**, 751 (1987)

19   Y. Xie, P.M.A. Sherwood, *Chem. Mat.*, **2**, 293 (1990)

20   D. Anjo, M. Kahr, M. Khodabakhsh, M. Wanger, S. Nowinski, *Anal.   Chem.*, **61**, 2603

(1989)

21   P.M.A. Sherwood, C.J. Kozlowski, *J. Chem. Soc., Faraday Trans.* 1, **81**, 2745

        (1985)

22   P. Ehrburger, J.J. Herque, J.B. Donnet, *Proc. 4th London Inter. Carbon and   Graphite*

        Conf., 1974, Soc. Chem. Ind., London, 201 (1976)

23   R-Y. Qin, J-B. Donnet, *Carbon*, **32**, 2, 323 (1994)

24   J-B. Donnet, R-Y. Qin, *Carbon*, **31**, 1, 7 (1993)

25   W.P. Hoffman, *Carbon*, **30**, 3, 315 (1992)

26   J-B. Donnet, R-Y. Qin, *Carbon*, **30**, 5, 787 (1992)

27   W.P. Hoffman, W.C. Hurley, T.W. Owens, H.T. Phan, *J. Mat. Sci.*, **26**, 4545   (1991)

28   ASTM E902-93 published in Vol. 03.06, *1994 Annual Book of ASTM Standards.*

        American Society for Testing and Materials, Philadelphia (1994).

29   Suggested by Tom Schuerlein.

30   P.M.A. Sherwood, in *Practical Surface Analysis in XPS and AES, in Practical*

        Electron Spectroscopy, ed. by D. Briggs and M.P. Seah, Appendix 3, 555-586,

        Wiley, Chichester (1990)

31   A. Proctor, P.M.A. Sherwood, *Anal. Chem.*, **54**, 1, 13-19 (1982)
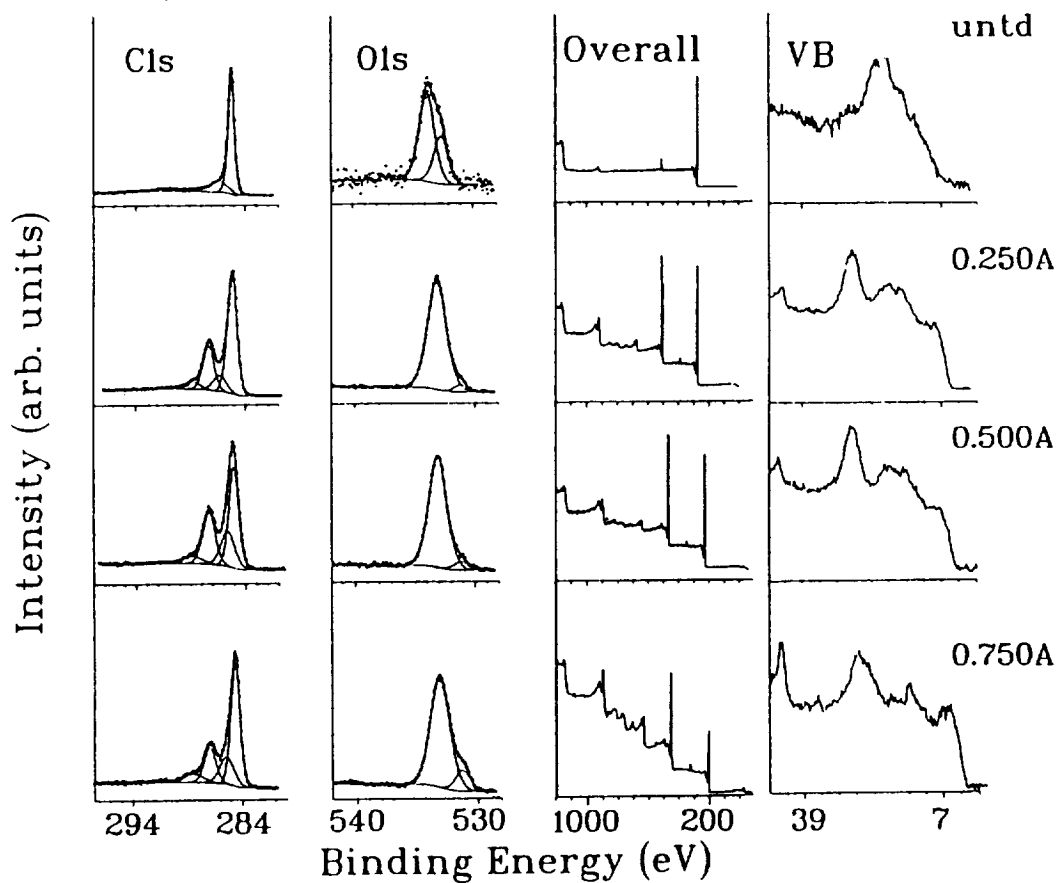
Figure 1 XPS spectra of anodically oxidized M40 carbon fibers using the fiber treatment line. Applied current is shown in Amps along the right side. "Untd" is the label for untreated M40 fiber.
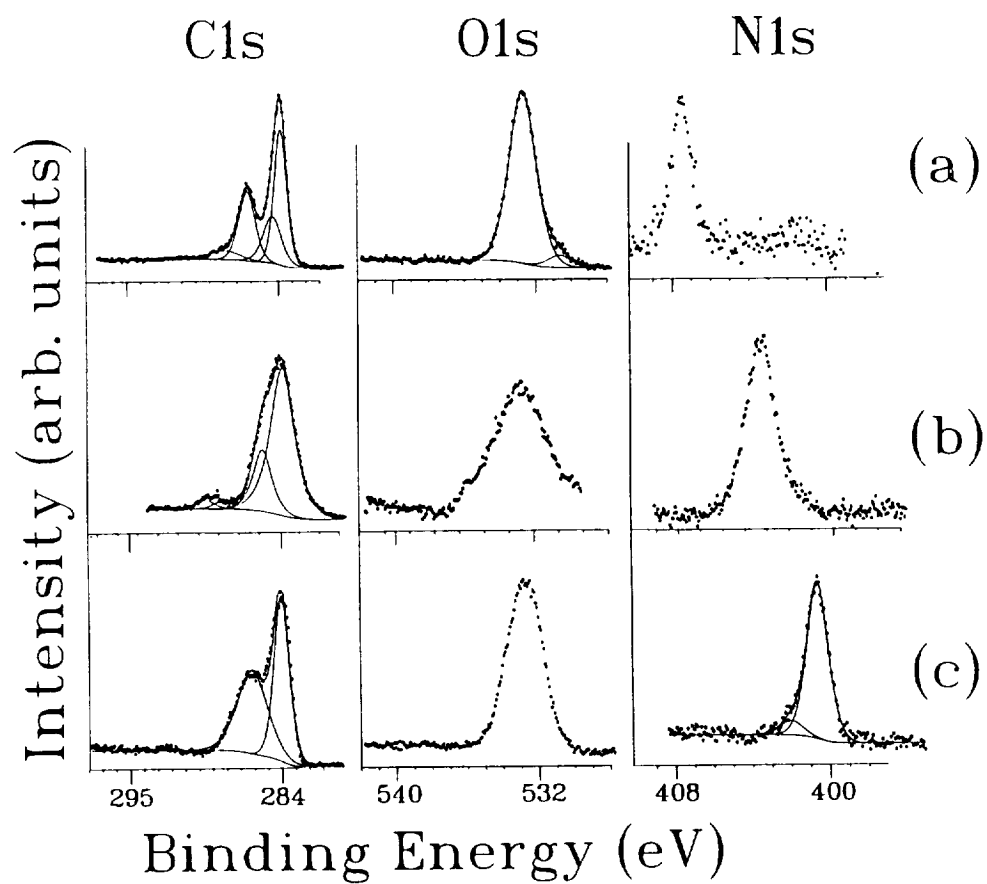
Figure 2 XPS core spectra for (a) M40 fiber anodically oxidized at 0.50A (N1s spectrum from 0.750A treated sample); (b) K3B resin powder; (c) K3B dip coated onto 0.50A oxidized M40 fiber
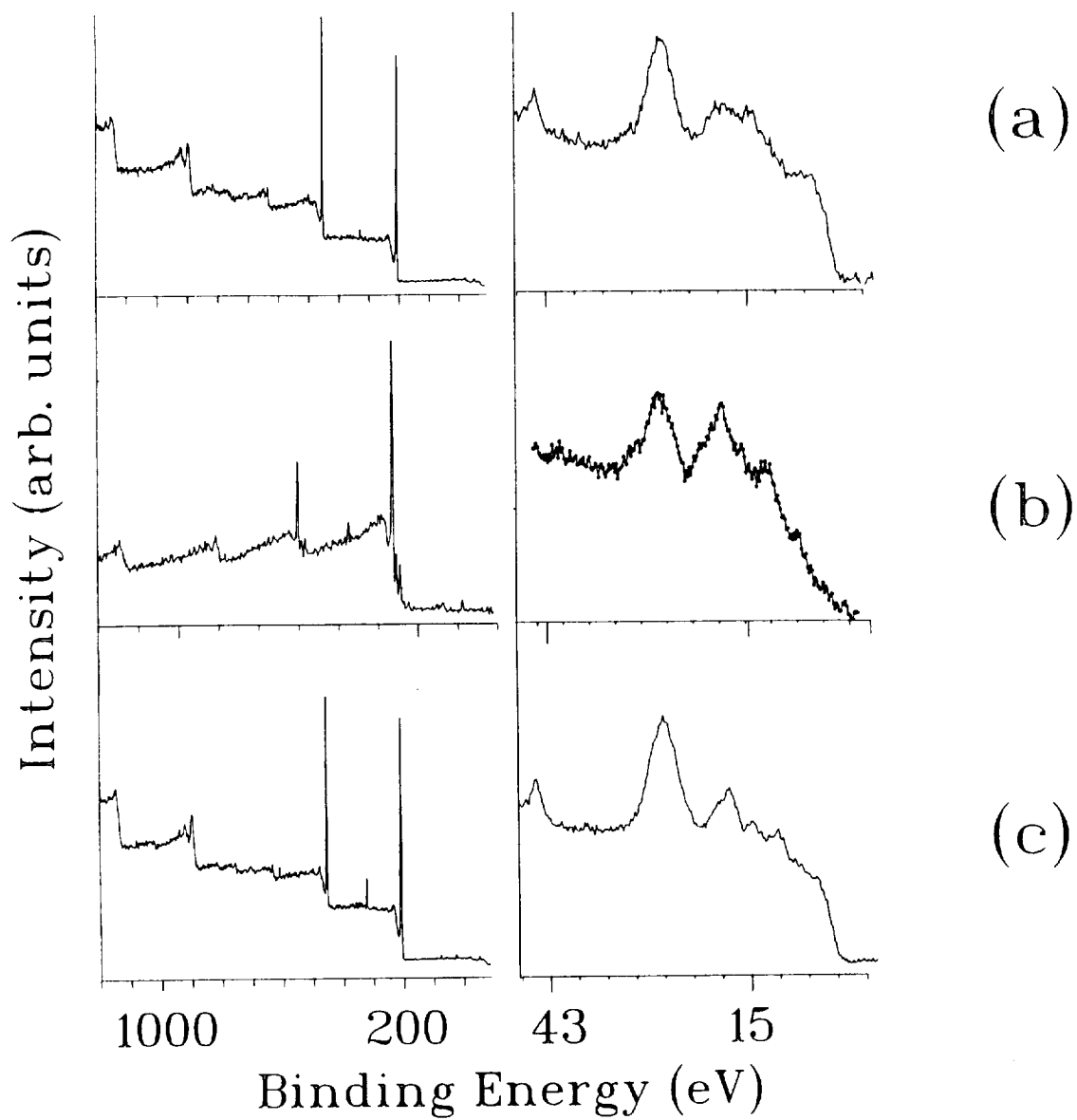
Figure 3 XPS survey and valence band spectra of (a) 0.50 A oxidized M40 fiber; (b) K3B powder; (c) K3B coated onto a 0.50A oxidized M40 fiber
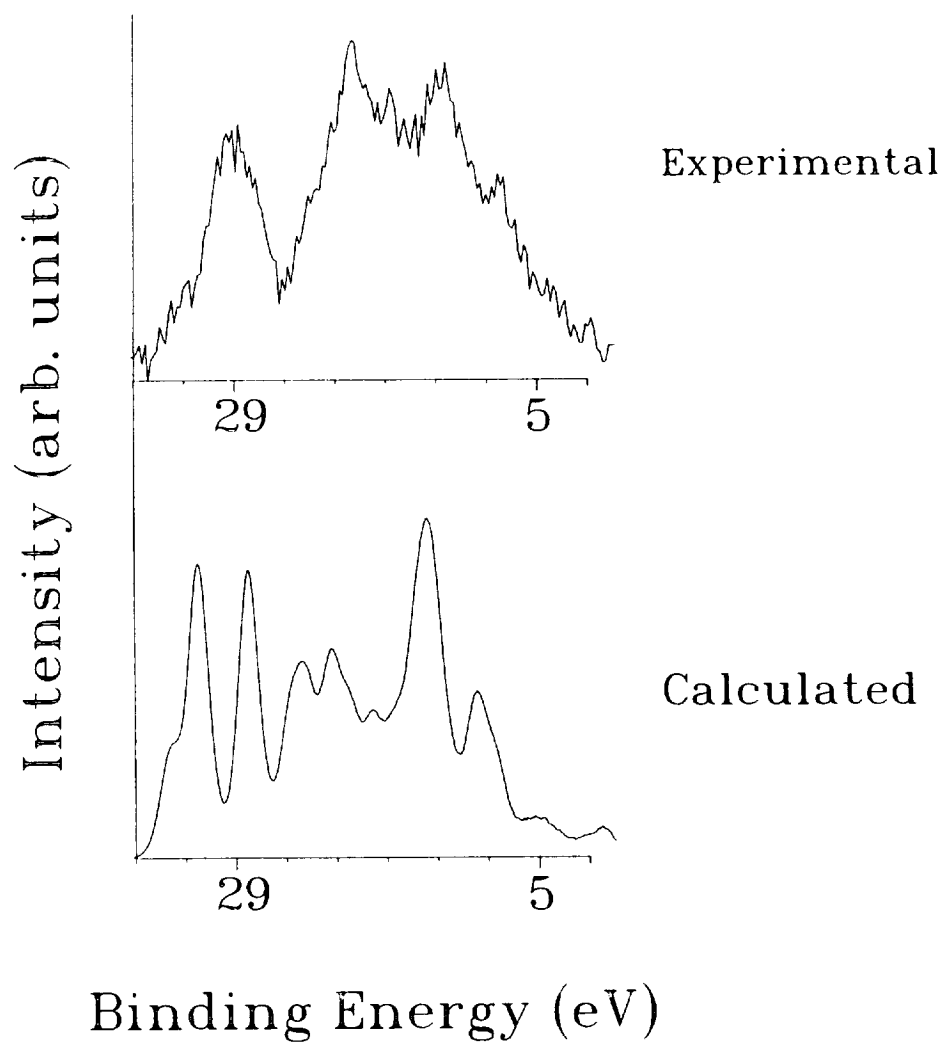
Figure 4 Comparison of the experimental and calculated valence band spectrum of K3B
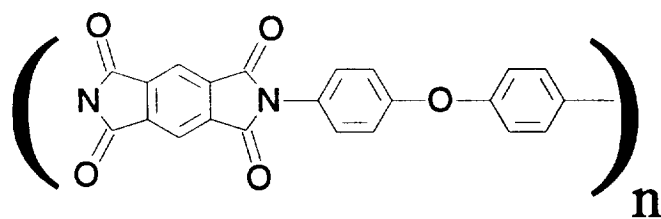
Figure 5 Proposed structure of Avamid® K3B.
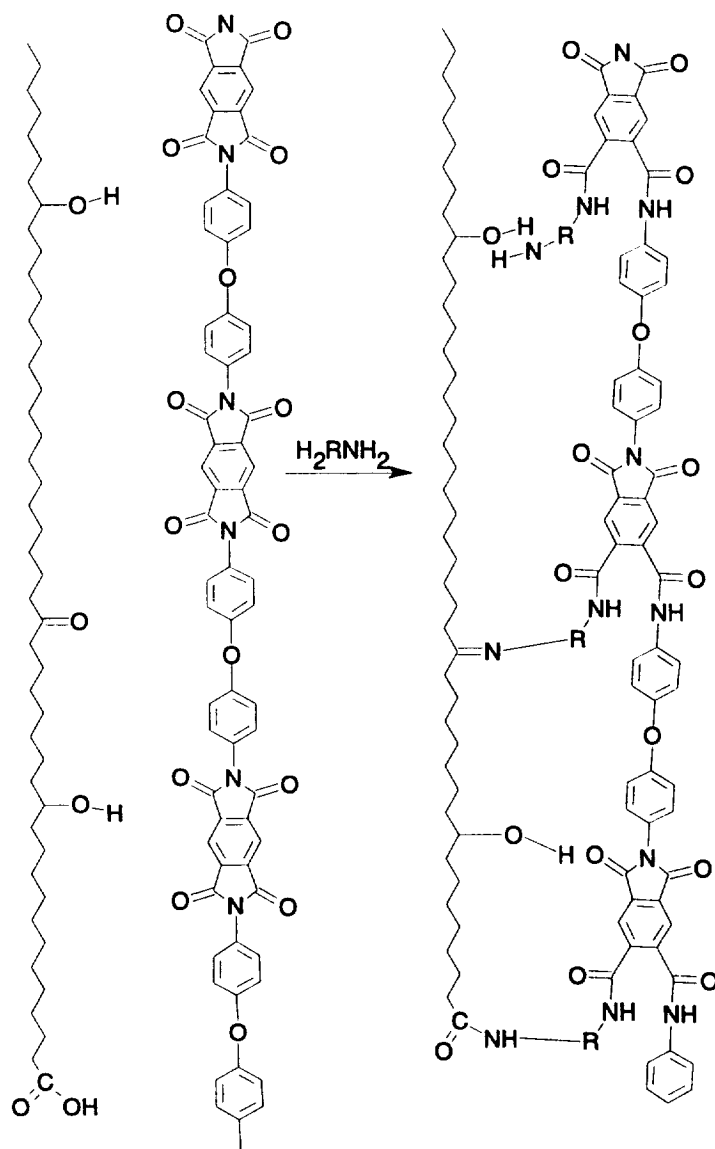
Figure 6 Proposed polyimid resin interaction with a carbon fiber.

56
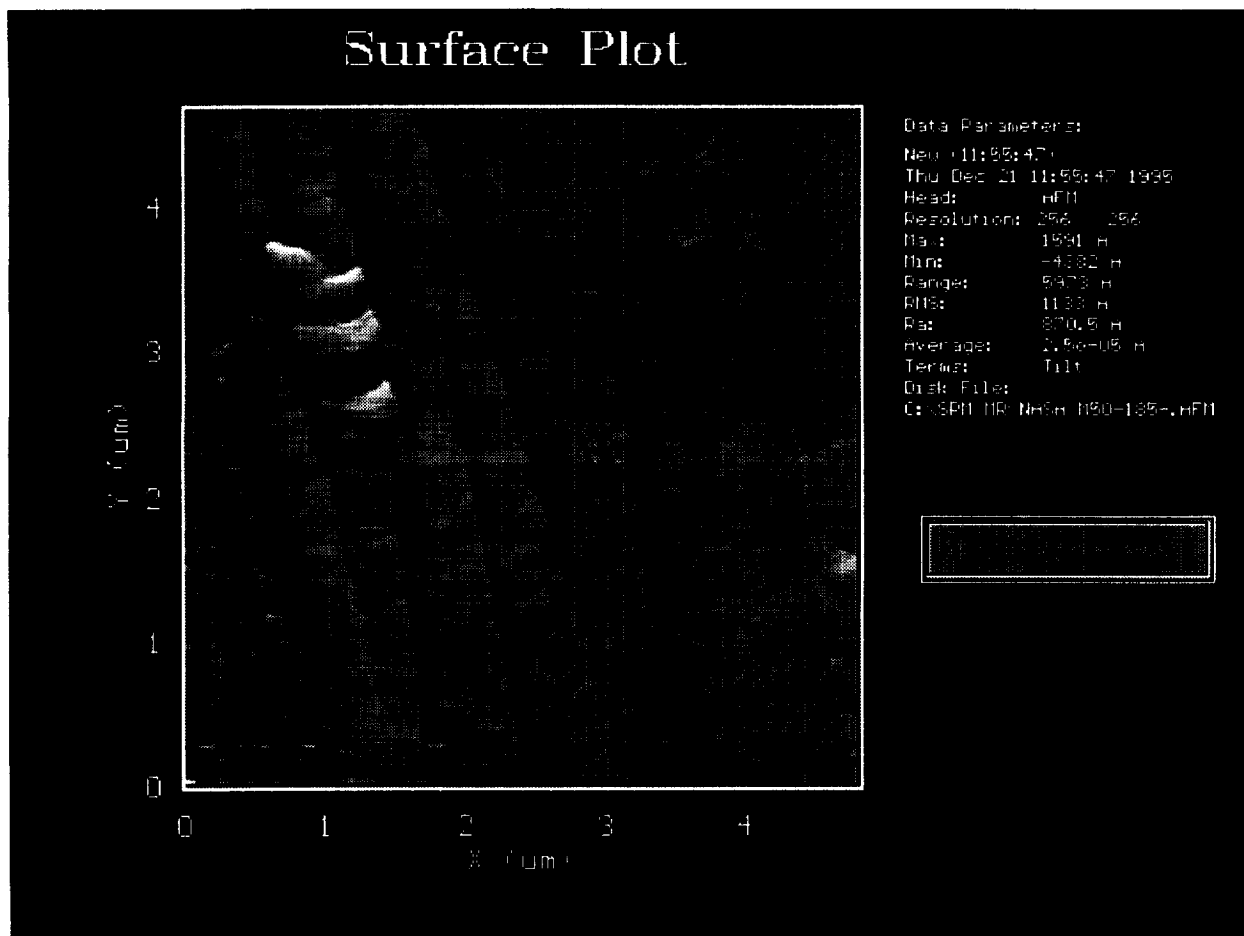
Figure 7 AFM 2-D shaded image of 0.185A anodically oxidized M40 fiber.
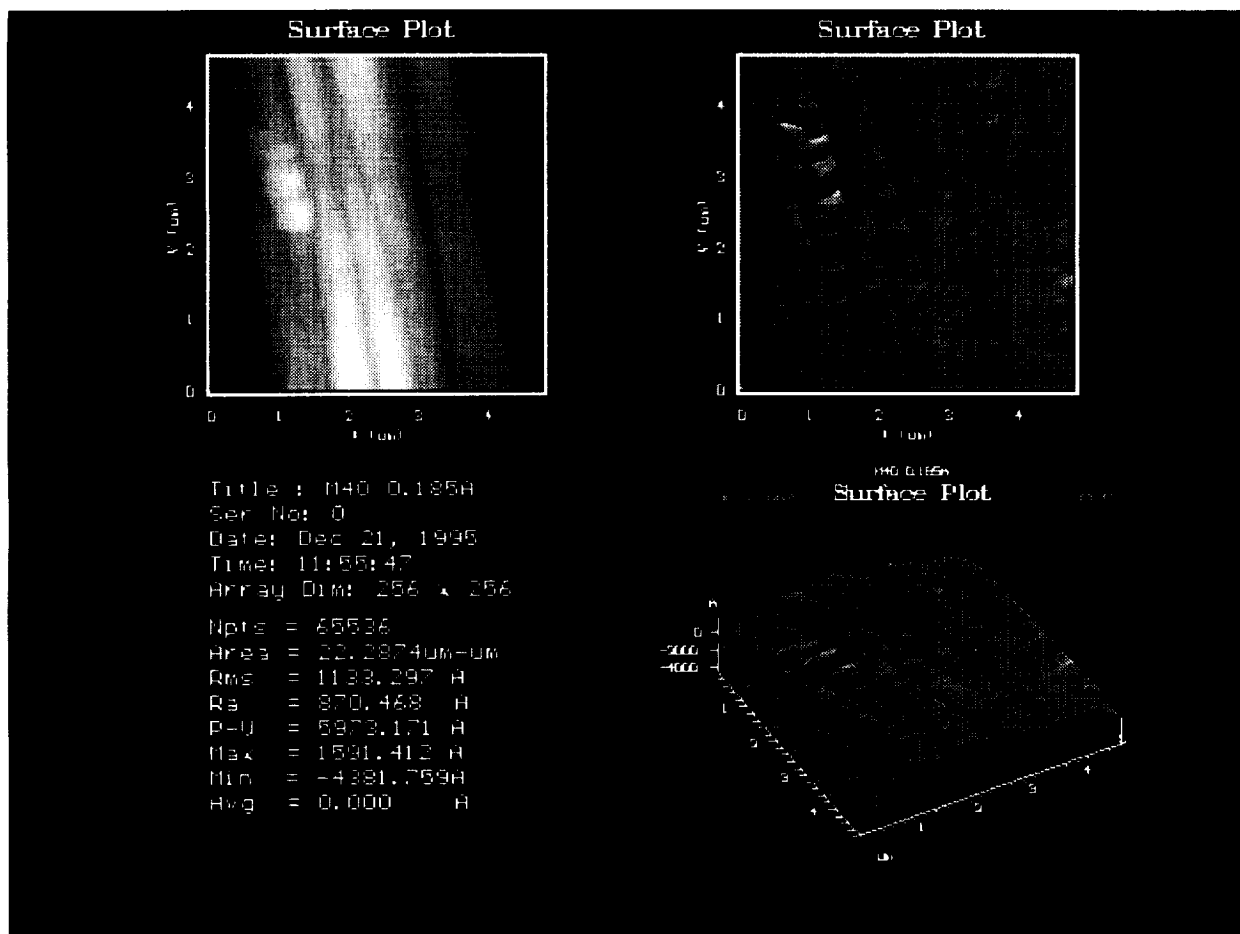
Figure 8 AFM images of 0.185A oxidized M40 fiber.
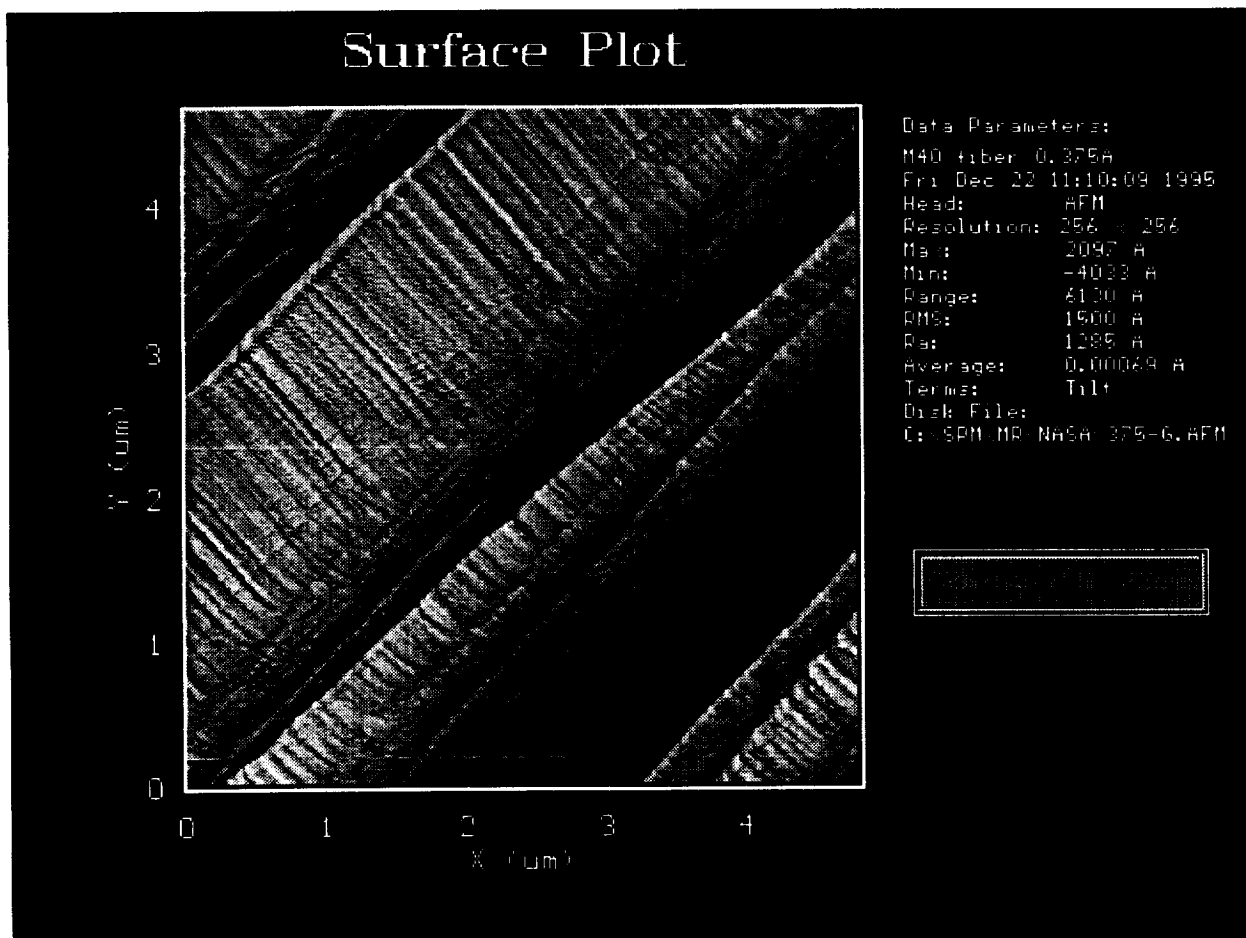
Figure 9 AFM 2-D image of 0.375 A oxidized M40 fiber.
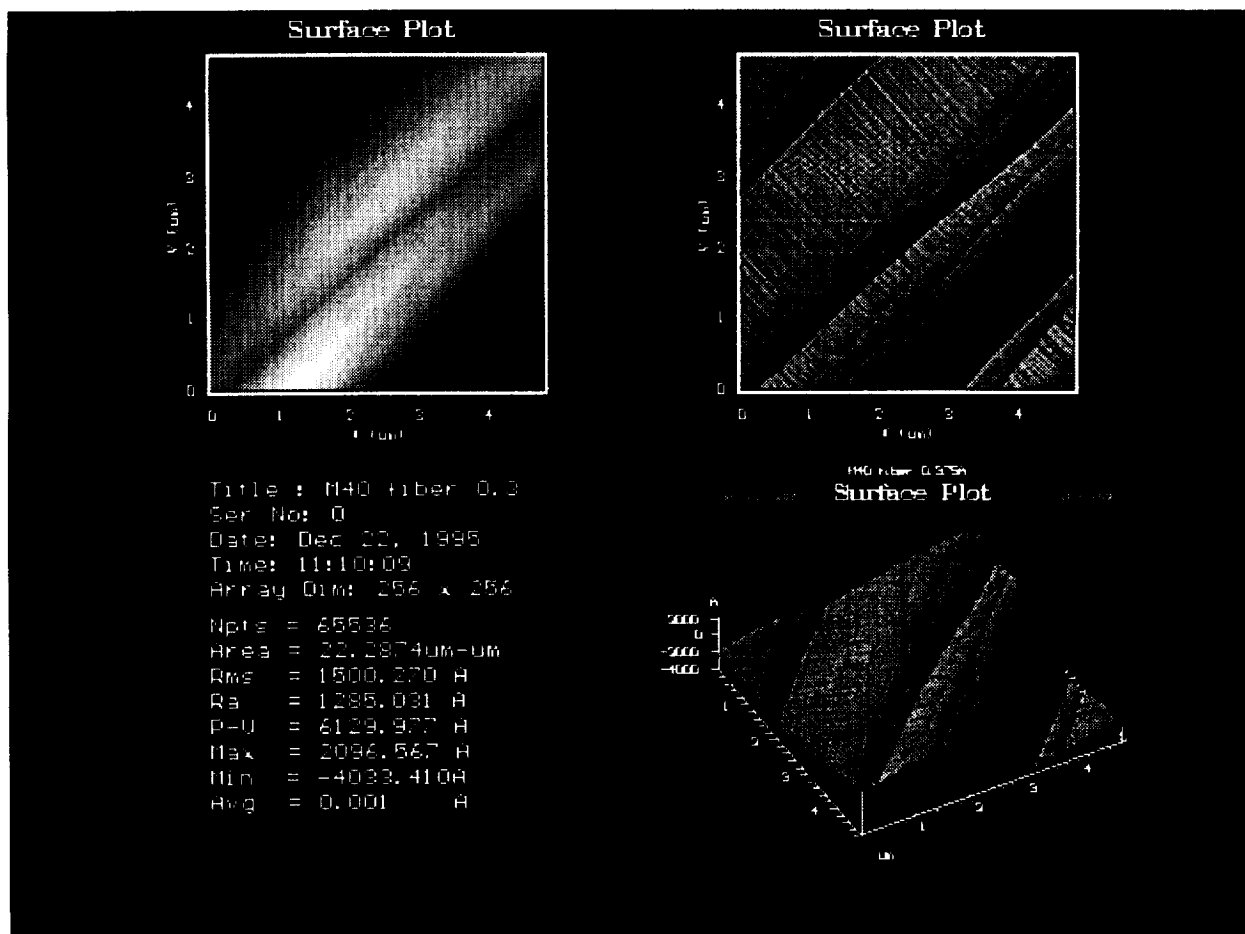
Figure 10 AFM images of 0.375A oxidized M40 fibers.
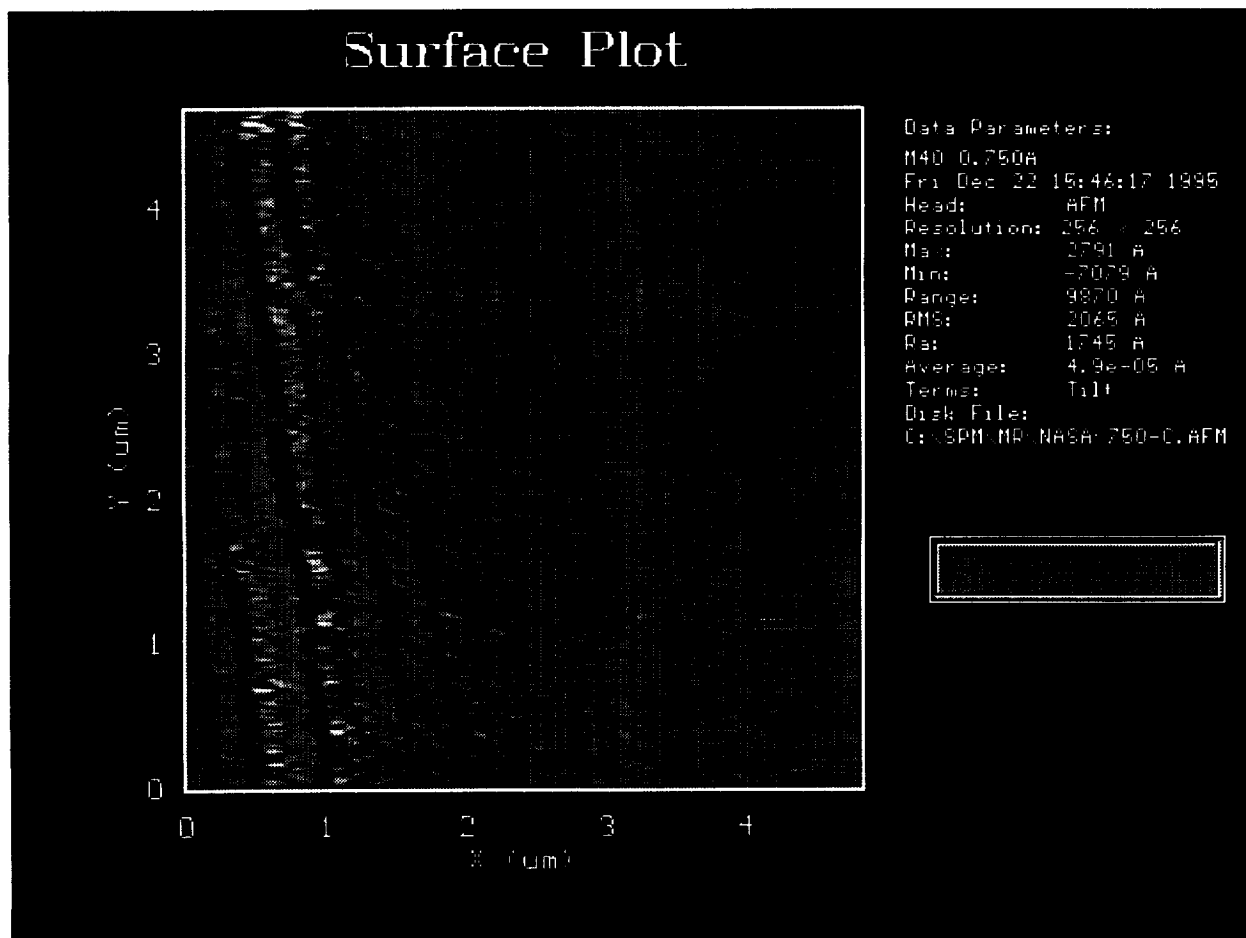
Figure 11 AFM 2-D image of 0.750A oxidized M40 fiber.
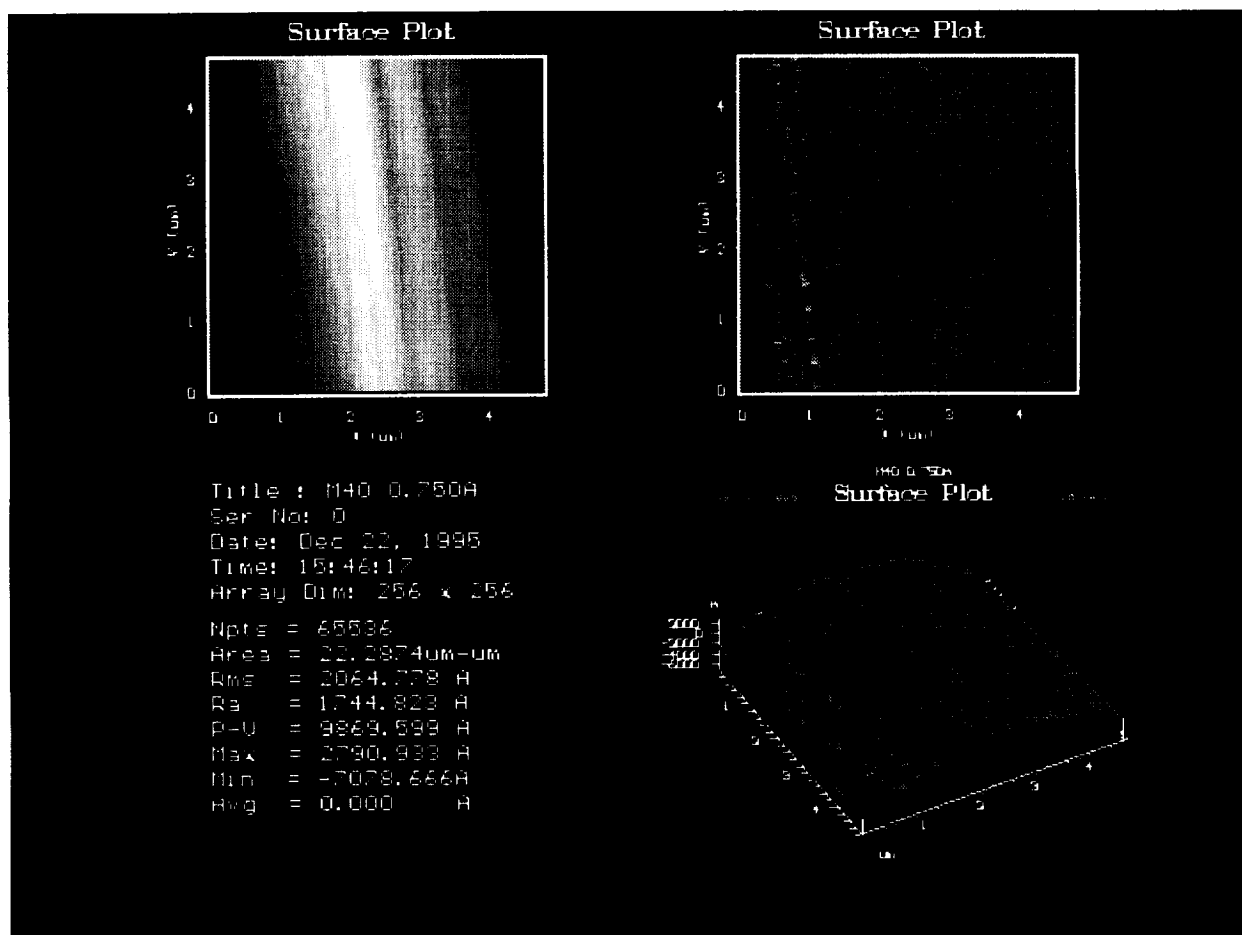
Figure 12 AFM images of 0.750A oxidized M40 fiber.

Thrust II

Advanced Composite Manufacturing

Youqi Wang, Assistant Professor of Mechanical Engineering, Kansas

State University, Manhattan, Kansas 66506

The manufacturing process for the laminated composite involves two steps. The first step is to incorporate fibers into a matrix, thus tow-prepregs are formed. Then, tow-prepregs are laid into unidirectional prepreg sheets, which are stacked to form laminated specimens by a pressing operation.

Last year a foam impregnation prepregging system was developed in the Department of mechanical Engineering at Kansas State University. Tow-pregs made from several kinds of fibers and thermoplastic resins were manufactured. The quality of the towpregs is examined.

1. Prepregging System Development

Fig.1 is an illustration of the system. First, the fiber tow moves through a tow spreader and is spread to a width of 2-3 inches. Then aqueous foam, as a carrier medium, is applied to the moving tow. The moving tow passes through a tube furnace and is then taken up by a rotating spool. The system includes four major devices: a pneumatic yarn spreader, a foam generating and supplying system, a tubular furnace and a product-take-up system. The prepregging process can be divided into four sub-processes: spreading yarn, applying matrix onto fiber, drying and curing the prepreg, and taking-up the final prepreg.

a. Spreading yarn:

Spreading the yarn helps achieve an adequate impregnation. The structure of the yarn spreader is shown in the Fig.2. The spreader consists of three pieces: a cover plate, a middle plate with several air slots and an air box. The yarn is placed between the cover plate and the middle plate. During the operation, the pressured air enters the air box from the pneumatic tubes connected to two sides of the box. Then, air is forced to pass through slots on the middle plate and then flows parallel with the yarn path. Consequently, the yarn is spread as shown in Fig.2.

b. Applying matrix onto fiber:

An aqueous foam, which carries the matrix powder, is then applied onto the spread yarn. The aqueous foam is produced by the following procedure: Firstly, a suspension is made from resin powder and water. A surfactant is added. Then the suspension is sent to a foam generating system, which is shown in Fig.3. This system includes a mixer, a resin pump and a pneumatic air supply. The suspension and pressured air are mixed generating foam.. The matrix powder sticks onto the foam's surface . The aqueous foam, as a carrier medium, is applied to the spread tow. A doctor blade is placed in front of the foam applicator in order to control the fiber volume fraction.

c. Drying and curing

The yarn then moves through a tube furnace. The temperature inside the furnace is kept slightly higher than the melting point of the matrix. The water and most of the surfactant within the suspension are removed in the tube furnace. The aqueous foams collapses. The resin powder melts and uniformly distributes onto the fiber. Thus, the towpreg is produced inside the furnace.

d. Taking up product:

The product take-up system is shown in Fig.4. This system includes two speed control motors. One is to control the linear motion of the spool and the other the rotating rate of the spool. The tow-preg is wound on the spool uniformly.

2. Test Runs of the tow-preg system

We started with available fibers and matrices. In our test runs of the tow-pregging system, samples of tow-pregs, made from IM7/polyester (thermoplastic) and E-Glass/polyester(thermoplastic), have been produced. Matrix suspensions with various surfactants and concentration were employed. Different processing rates and processing temperatures were tested. The effect of specific surfactants and the other processing parameters on the quality of tow-pregs is being examined. The fiber volume fractions of the tow-pregs have been controlled to be between 40%-70%. In addition, Hercules donated unsized AS4 fibers and Witco Corporation donated several surfactants. Two carbon fibers, unsized AS4 fiber and polyimide sized T650 fiber, will be used to make carbon fibers/polyimide resin prepregs in the coming month. Manufacturing related problems, such as the removal of the surfactant, the process rate

and the processing temperature, will be verified. These test runs will provide useful data for the

processing of the IM7/K3-B prepreg.
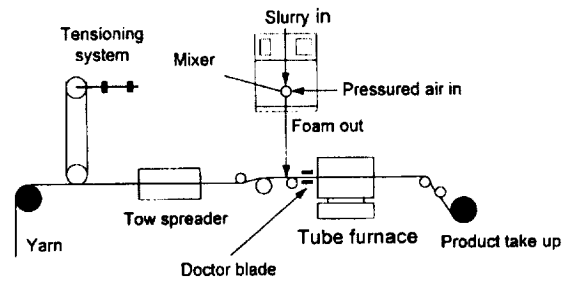
Fig.1 Prepregging system
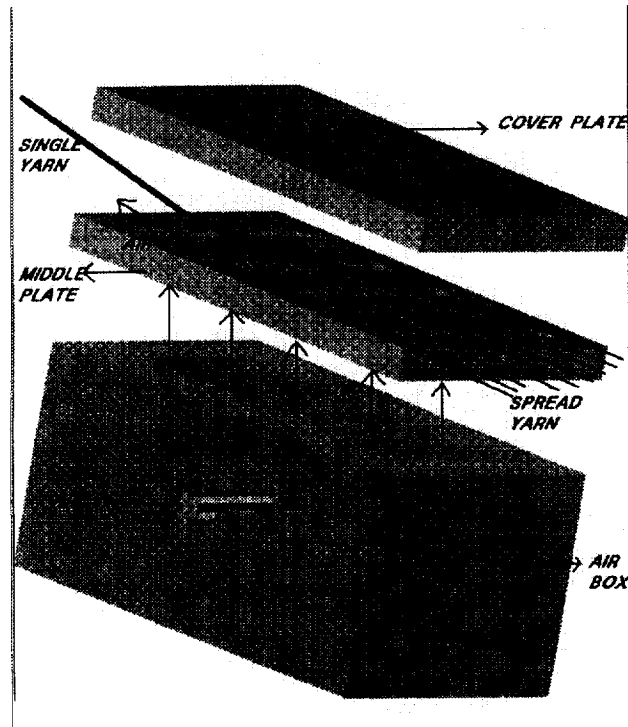
Fig.2 Yarn Spreader
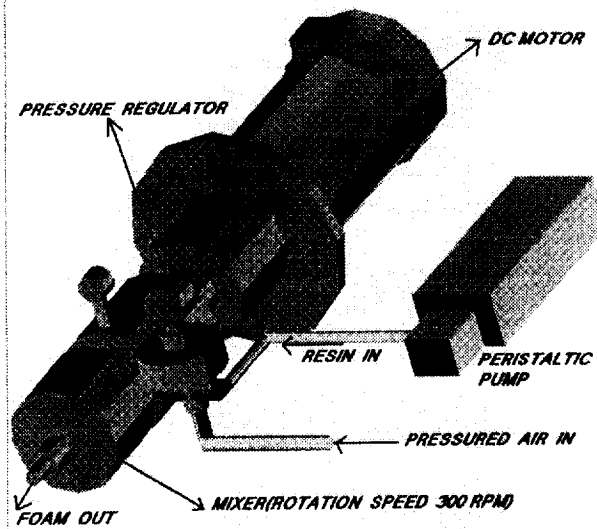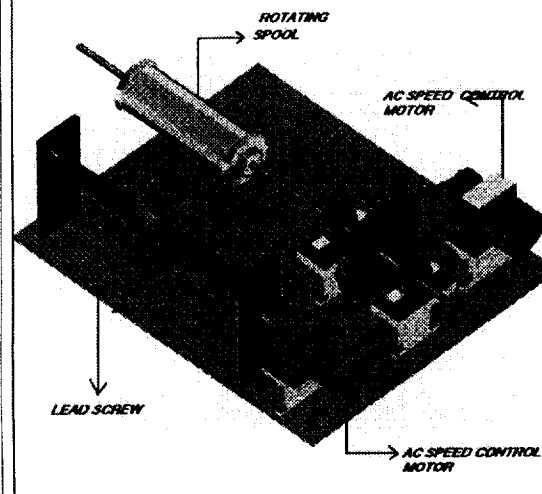
Fig.3 Foam Generating System

FIg.4 Prepreg Take-up System

Thrust III

Computational Models

James E. Locke, Associate Professor of Aerospace Engineering, 2004 Learned Hall, The University of Kansas, Lawrence, Kansas 66045
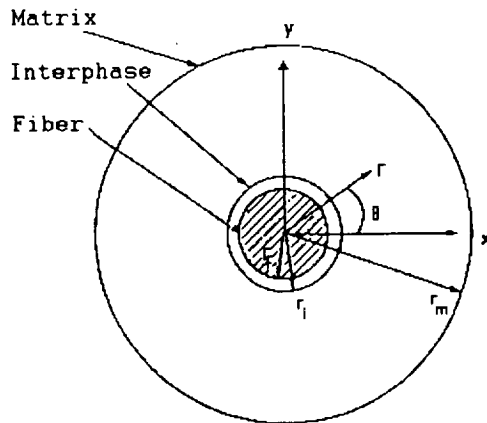
Fig. 1 (from reference 4)

The computational modeling research objective was to develop micromechanical models that account for the effects of fiber surface treatment (and chemistry). Much of the work in this area is based on the concentric cylinder model (CCM)1-4 shown in Fig.1. This model consists of a coated fiber embedded in a matrix, where the fiber coating plus a small amount of material on either side of the coating are treated as interphase.This interphase region accounts for the fiber surface treatment and the resulting material property changes that occur near the fiber-matrix interface. Pagano and Tandon1 developed an elasticity solution for the CCM and demonstrated that interphase properties can significantly alter stresses (at the fiber-matrix interface) and the composite material moduli. Carman et al.4 used a CCM to study the effect of fiber coatings on stress concentrations at the fiber-matrix interface. Fiber and matrix Young's moduli were held constant while the interphase modulus was varied. Their results demonstrate the significant effect of the interphase modulus—maximum stresses were reduced by a factor of 3. These models confirm previous results obtained by Sherwood [References]—surface chemistry and mechanical properties can be substantially changed through the use of surface treatment. Therefore, the CCM approach was chosen for the present study.

The above-mentioned previous studies were based on elasticity solutions with numerous simplifying assumptions, including homogeneous properties and perfect bonding. A recent study 5 used a finite element computational model to examine the effects of localized debonding and material property variations (in the radial direction). The results demonstrate that localized debonding produces significant increases in stresses near the interphase region. Based on these results it is obvious that one of the goals of fiber surface treatment should be to minimize localized stress concentrations due to changes in material properties and debonding.

The present research has focussed on developing a flexible modeling approach that incorporates localized effects. Therefore, the NASTRAN finite element code was chosen as a computational modeling tool. Preliminary models were constructed for two problems: 1) a fully three-dimensional CCM, and 2) a two-dimensional model. A cross-sectional view of the first model is shown in Fig. 2.This model was developed both to compare with previous results1 and to prepare for future comparisons with experimental results.

Comparisons with previous elasticity results are shown in Figs. 3 through 5. These results
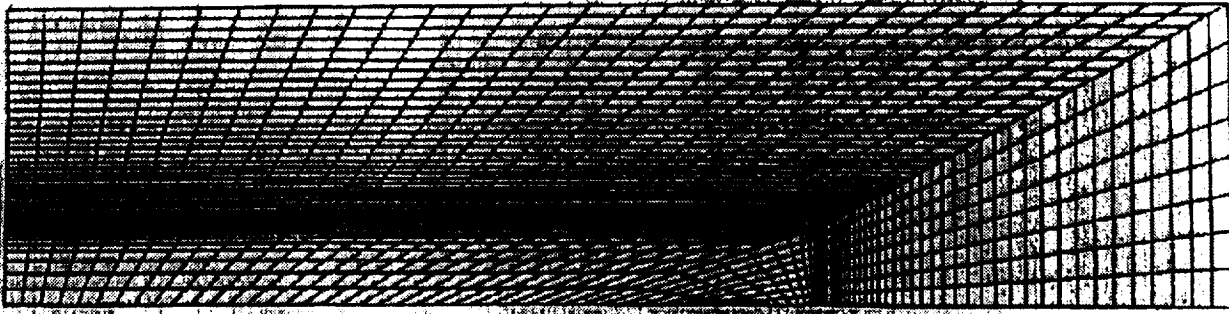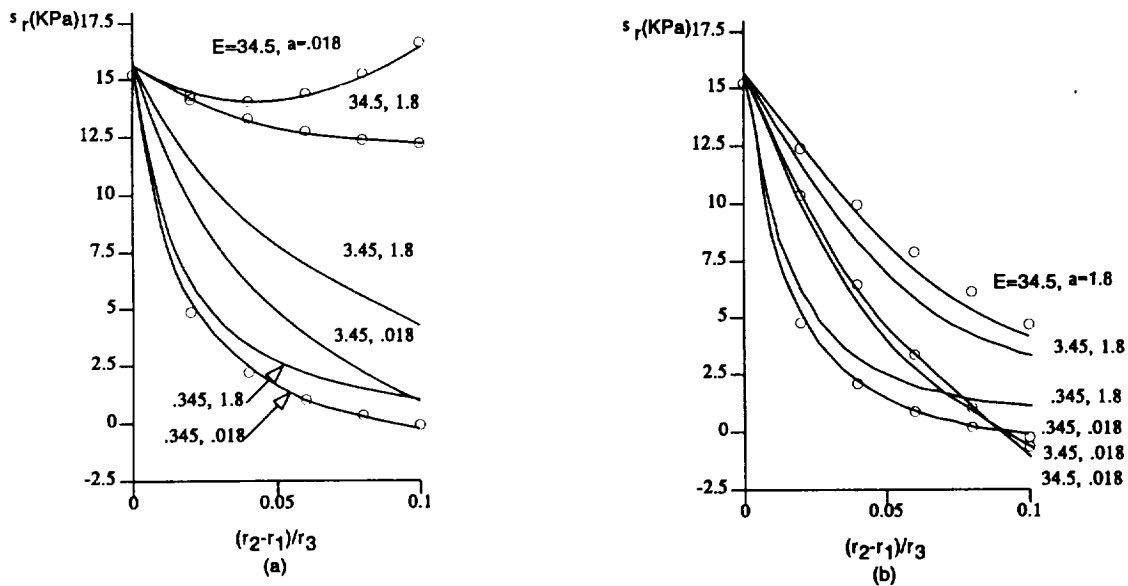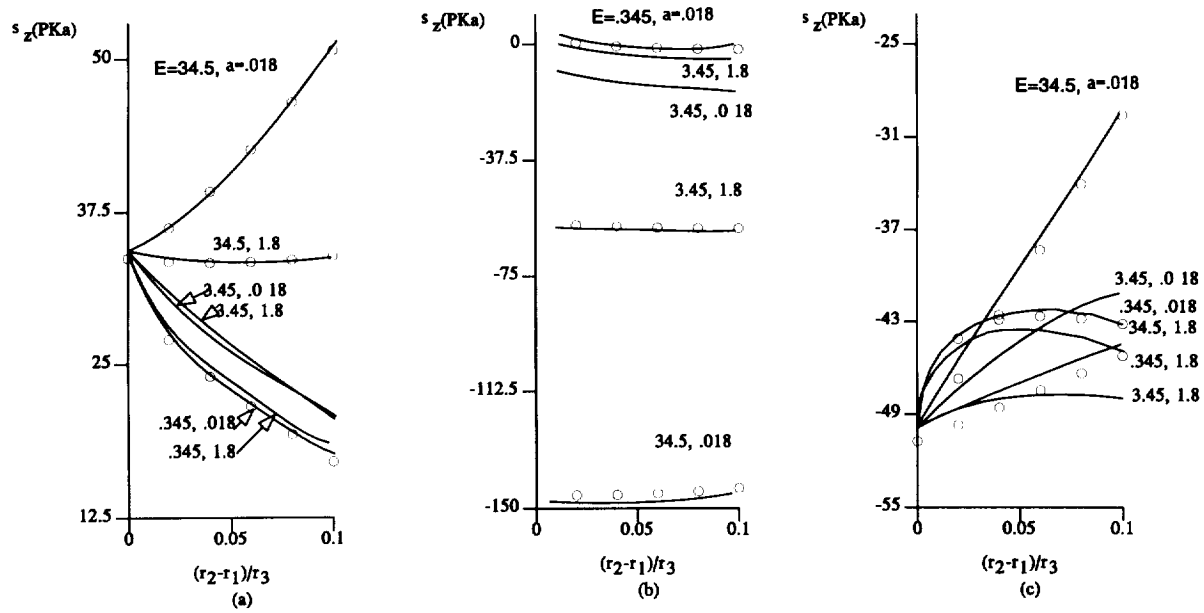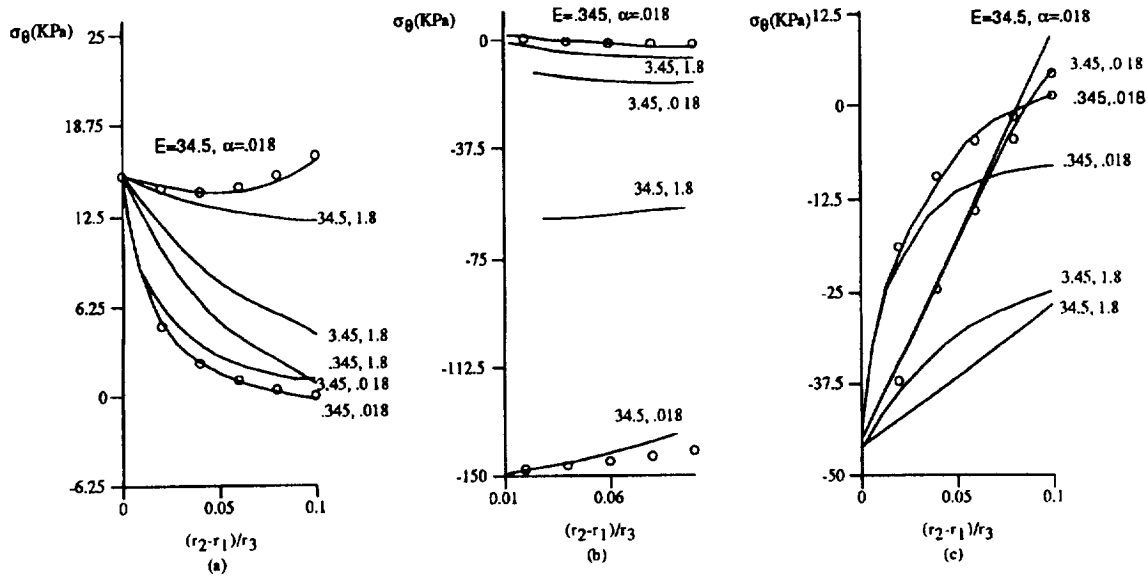

Fig. 2

demonstrate that the three-dimensional model is sufficiently refined to determine localized stresses.

● Fig. 3. Radial stress at (a) fiber-coating interface; and (b) coating-matrix interface for Nicolan/BMS composite under a uniform temperature change, DT=1°C. (E: coating modulus (GPa), a :coefficient of thermal expansion of coating(1/1,000,000)°C. Continuous lines from Ref. 1 circles from FEA modeling.

69

Fig. 4. Longitudinal stress inside (a) fiber; (b) coating (c)matrix for Nicolan/BMS composite under a uniform temperature change, $DT=1°C$. (E: coating modulus (GPa), ^{a} :coefficient of thermal expansion of coating(1/1,000,000/ °C.). Continuous lines from Ref. 1 circles from FEA modeling.

Fig. 5. Hoop stress at inside (a) fiber; (b) coating (c) matrix for Nicolan/BMS composite under a uniform temperature change,$\Delta T=1°C$. (E: coating modulus (GPa), α:coefficient of thermal expansion of coating(1/1,000,000) °C.). Continuous lines from Ref. 1 circles from FEA modeling.
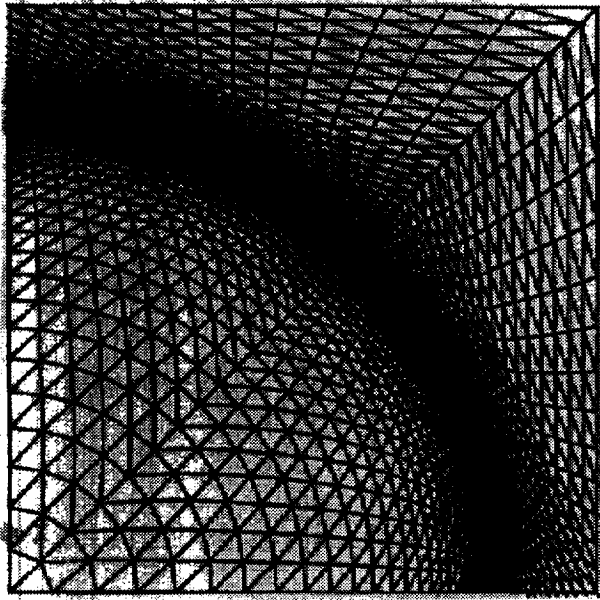
70

Fig. 6

A two-dimensional model was also used to study the effect of localized material property variations. This model is shown in Fig. 6, and an example stress field is shown in Fig. 7. The localized stress peaks correspond to areas with material property variations. The present results are for variations of the interphase modulus in the angular direction. Interphase properties are constant in the radial direction. Fiber and matrix properties are constant throughout.

In summary, micromechanical finite element models that account for the effects of fiber surface treatment (and chemistry) have been developed. The three-dimensional results compare favorably with previous elasticity solutions. The results shown in Fig. 7 provide an example of localized stress peaks due to material property variations.
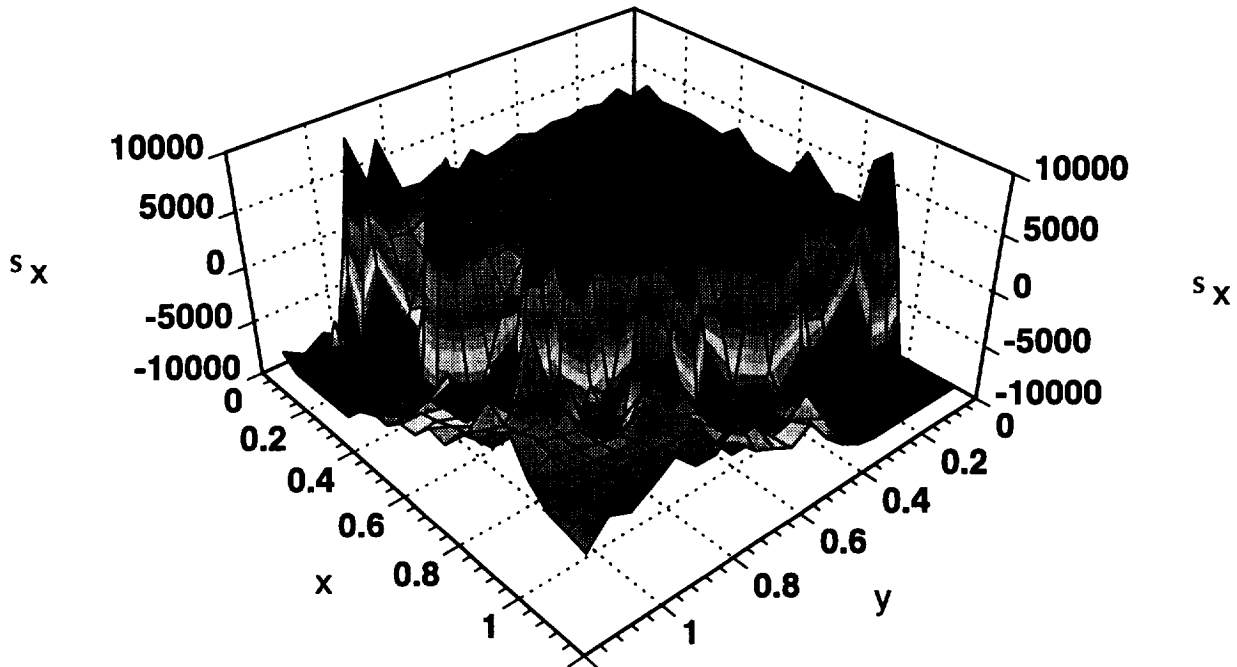

Fig. 7 FEA results of normal stress field , for Nicolan/BMS composite under an uniform

71

temperature change of 1 degree of celcius, thermal expansion of coating = 1.8e-6. Coating elastisity properties were subjected to a change in the angular direction in a sinusoidal fashion with the frequency of 6 .

Future work will focus on comparisons with Lease and Tomblin experimental results and identifying material property variations that are produced by the fiber surface treatment process. Once a method has been developed for identifying localized property variations, computational models can be developed to determine what
property variations produce the most favorable stress field; thus providing a direct method for evaluating the micromechanical performance of fibers subjected to various surface treatment processes.

References

1. N. J. Pagano and G.P. Tandon, "Elastic Response of Multi-directional Coated-fiber Composites," Composites Science and Technology, Vol. 31, 1988, pp. 273-293.
2. N. J. Pagano, "Axisymmetric Micromechanical Stress Fields in Composites," IUTAM Symposium on Local Mechanics Concepts for Composite Material Systems, Blacksburg, Virginia, 1991.
3. G.P. Tandon, "Use of Composite Cylinder Model as Representative Volume Element for Unidirectional Fiber Composites," Journal of Composite Materials, Vol. 29, No. 3, 1995, pp. 388-409.
4. G.P. Carman et al., "Optimization of Fiber Coatings to Minimize Stress Concentrations in Composite Materials," Journal of Composite Materials, Vol. 27, No. 6, 1993, pp. 589-612.
5. R. M. Hackett and M. A. Labadi, "Computational Simulation of Fiber/Matrix Debonding in Filamentary Composite Material Systems," 38th International SAMPE Symposium, May 10-13, 1993.

Thrust IV

Mechanical Evaluation of Fiber/Matrix Adhesion I

Kevin B. Lease, Assistant Professor of Mechanical Engineering, Kansas State University, Manhattan, Kansas 66506

Introduction

This phase of the project involves mechanical testing to evaluate the effect of the fiber surface treatment on the mechanical behavior of the composite material. These tests will be performed on composite specimens manufactured using untreated carbon fibers, commercially treated carbon fibers and carbon fibers treated during Thrust I of this project. This evaluation will be carried out at both the micomechanical and macromechanical levels and will not only provide a comparative evaluation of the fiber surface treatment process but will also provide input properties and experimental verification testing for the computational modeling phase of this project (Thrust III).

Mechanical Testing

Micromechanical testing will employ single filament specimens and will thus provide a more direct evaluation of the effect of the fiber surface treatment on the quality of the fiber-matrix adhesion. Since the fabrication of these specimens does not require composite laminate panels, this type of evaluation is also attractive as a first step because it can be performed prior to the completion of the manufacturing stage of this project (Thrust II). This will allow essentially immediate feedback to Sherwood concerning the effect of the fiber surface treatment on the fiber-matrix adhesion. The primary testing technique used in the micromechanical investigations will be the single fiber fragmentation test. This technique involves performing a tensile test on a small specimen consisting of a single carbon filament embedded within a matrix coupon. By analyzing the fracture process that occurs in the carbon filament during the application of the tensile loading, important characteristics concerning the interfacial shear strength and the dominant damage mechanisms can be determined. The experimental set-up required to perform this delicate micromechanical test has been developed and evaluated in the Mechanical Testing and Evaluation Lab at KSU. The single fiber fragmentation tests will be performed under a zoom field stereoscopic microscope fitted with large working distance objective lenses, a camera, and a polarizing attachment so that the entire fiber fracture process can be observed and recorded during the single fiber fragmentation test. Scanning electron microscopy will be performed to analyze the fractured single filament test to be successful, the matrix material must be semi-transparent (for thickness up to approximately 1/16") and must exhibit a strain to fracture of approximately 3 to 4 times that of the single fibers. The K3B matrix material that is the focus of this project has been formed into a thin sheet and appears to satisfy the first

73

criterion. Neat resin samples will be formed to obtain the strain to fracture of the matrix material.

The macromechanical evaluation of the fiber surface treatment effect will consist of an evaluation of the shear response of the composite material through the use of ASTM standard test specimens. Although this type of test produces a somewhat indirect evaluation of the fiber-matrix adhesion, it is attractive because it provides familiar design-related composite properties. The test that will be employed in this phase of the mechanical evaluation process is the Iosipescu shear test. The Iosipescu shear tests will be performed as directed in ASTM Standard D5379. Specimens used in these tests will be machined from composite laminate panels manufactured in Thrust II of this project. Test fixtures necessary to perform these ASTM standard tests are either already in place at KSU or are in the process of being manufactured. The data collected from these tests will not only provide a comparative evaluation of the effect of the fiber surface treatment but will also produce a rather comprehensive characterization of the shear properties of the fiber/matrix system under investigation in the project. The members of the High Speed Research program at NASA Langely suggested that the macromechanical evaluation should also ensure that the fiber surface treatment tailored to maximize the composite shear properties mentioned above does not at the same time significantly degrade other aspects of the mechanical response. Based on this suggestion, ASTM standard tensile tests will be performed during each phase of the fiber surface treatment iterative process.

Mechanical Evaluation of Fiber/Matrix Adhesion II

John S. Tomblin, Assistant Professor of Aerospace Engineering, The Wichita State University, Wichita, Kansas 67260-0093

Status Report

Wichita State University's primary goal of the current project was the generation of useful techniques to aid in the evaluation of the macromechanical behavior of advanced fiber surface treatments for carbon fiber reinforced composites. In cooperation with research members from Kansas State University and the University of Kansas, this phase of the project involved developing testing techniques to evaluate the effects of the different surface treatments with respect to the global macromechanical properties of the composite.

Various techniques have been proposed to study the effect of fiber surface treatments with respect to the global composite mechanical properties [1]. These tests have incorporated a variety of test methods aimed primarily at quantifying the shear, transverse tension and longitudinal compression. Unlike the micromechanical tests which independently evaluates the fiber/matrix adhesion based upon tests on a single filament, the macromechanical tests will provide an indication of actual design-related performance characteristics for a fiber reinforced composite. The current investigation phase of this project performed by Wichita State University and the National Institute of Aviation Research was aimed primarily at the shear behavior which has been shown to be one of the major factors which influence the fiber/matrix bond performance [2].

Although many test methods provide shear response data for fiber reinforced composite materials, concerns still exist in the testing community as to which method best produces credible data, generates an acceptable stress field during testing and is relatively insensitive to specimen fabrication and experimental test setup. Torsion of hoop-wound thin-walled tubes generates a stress state ideal for pure shear response, however the tubular specimens are difficult and expensive to manufacture and extreme care must be taken when loading [3]. The Iosipescu and the ± 45° tension tests are preferred methods by industry standards, rendering relatively consistent data. The Iosipescu specimen, though producing a favorable shear response in both modulus and strength, comparable to a torsion tube, remains sensitive to specimen imperfections and is traditionally manufactured via a prepreg layup technique. The ± 45° tension test produces relatively good results for the shear modulus but strength values remain unpredictable and commonly fall well below other traditional methods [3]. Fabrication methods to produce the ± 45° tension test specimens also traditionally involve prepreg fabrication techniques. Solid rod specimens have also been used in torsion to characterize the nonlinear shear behavior but are not attractive due to nonuniform

stress field produced [4]. Figure (1) shows some comparative results for the different shear testing methods taken from reference [3].

Based upon these results, the current effort was focused towards providing methods to produce reliable macromechanical behaviors in shear to evaluate the performance of the fiber/matrix adhesion. Since the development of prepreg type specimens (Iosipescu and ± 45° tension) require the completion of the manufacturing stage of this project, alternative methods for producing the macromechanical shear response without the use of prepreg were studied. Primarily, for this phase of the project, both the torsion tube and solid rod torsion test were investigated. Both of these test methods require only the use of towpreg or wet filaments for specimen fabrication. The philosophy in choosing both of these methods is that fiber surface treatments may be readily changed and its effect on the global macromechanical properties investigated without consuming massive quantities of fiber and resin and manufacturing time (i.e., bypassing the prepreg stage of the project). Since both test methods require the use of the torsion machine, a small scale torsion machine was designed and built for the current investigation.

Since the treatments on the K3B resin system were not fully ready for a complete trial run, another resin system was chosen for the initial baseline study. The purpose of this study was to calibrate the testing setup to approved ASTM testing methods and produce reliable shear responses. For the purpose of this baseline study, 3501-6 resin, in raw form, was obtained from Hercules, Inc. along with IM7 carbon fibers. In addition, 3501-6/IM7 prepreg was also obtained to perform the baseline ASTM type tests. The treatments of the fibers were standard epoxy surface treatments and sizing. Hence, the baseline study will not be used to show any effects of fiber/matrix interaction but simply be used to validate the testing methodology.

Progress-to-Date

- 3501-6 resin obtained from Hercules, Inc.
- IM7 fibers obtained in 12k tows
- 3501-6/IM7 prepreg obtained
- ASTM specimens fabricated and tested (Iosipescu and ± 45° tension) and nonlinear shear curves obtained (these will be used as the baseline for the torsion machine validation)
- torsion machine designed and fabricated along with computerized data acquisition for both angle-of-twist and torque measurements
- filament wound torsion tubes fabricated from epon 862 (problems encountered with the viscosity of 3501-6 - additional work needed for high viscosity resin systems)
- filament wound tubes (epon 862/Grafil) tested and testing procedures obtained

76

- solid rod specimens (3501-6/IM7) specimens fabricated using a modified pultrusion process (several different diameters)
- torsion tests begun along with analytical procedures for transforming the nonuniform torque/angle-of-twist data to traditional shear stress/strain relationship

References

(1) Madhukar, M.S. and Drzal, L.T. (1993) "Fiber-Matrix Adhesion and Its Relationship to Composite Mechanical Properties," *Journal of Materials Science*, Vol. 28, pp. 569-610.

(2) Madhukar, M.S. and Drzal, L.T. (1991) "Fiber-Matrix Adhesion and Its Effect on Composite Mechanical Properties : I. Inplane and Interlaminar Shear Behavior of Graphite/Epoxy Composites," *Journal of Composite Materials*, vol. 25, pp. 932-957.

(3) Chaterjee, S.N., Adams, D.F. and Oplinger, D.W. (1993) "Test Methods for Composites : A Status Report - Volume III : Shear Test Methods," *FAA Final Report DOT/FAA/CT-93/17, III,* Composite Research Group and the Material Science Corporation, Philadelphia.

(4) Chaterjee, S.N., Yen, C.F., Kessler, J.A. and Adams, D.F. (1993) "Inelastic Shear Response of Unidirectional Composites from Torsion of Solid Bars," *ASTM STP 1206,* ASTM, Philadelphia, pp. 53-69.
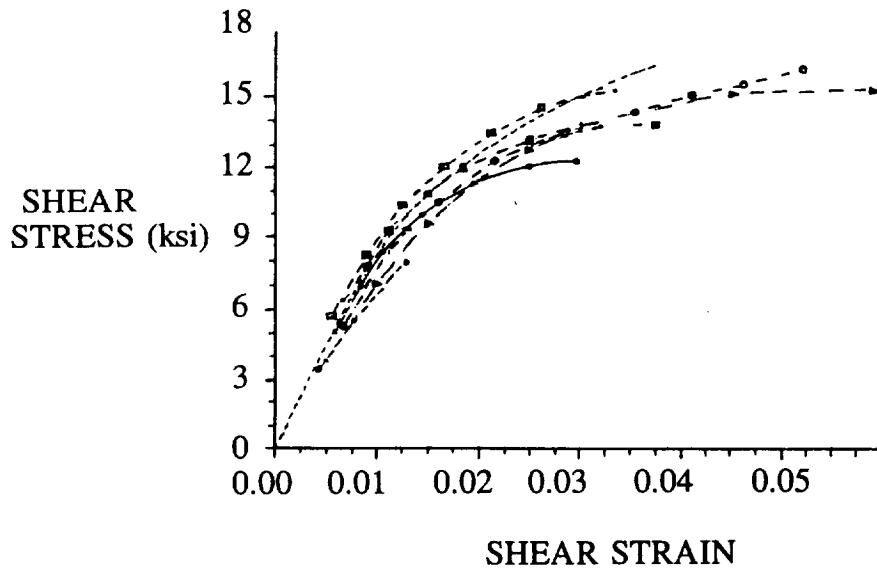
Figure 1 Representative shear response data from different inplane shear tests on unidirectional AS4/3506-1 specimens (see ref [3]).

Key:　　　　　　　-•-　(+45) Tension
　　　-►-　$(O)_{16}$ Iosipcscu
　　　-□-　$(O)_{18}$ Rectangular Rail
　　　-○-　$(O)_{18}$ Parallelogram Rail
　　　-●-　Torsion 0.23″ Dia. Bar
　　　---　Tor. 0.47″ wide　$(O)_{18}$ Rectangular Bar
　　　-•-　$(15)_{18}$ Off axis